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PHYSICO-CHEMICAL STUDIES ON PROTEINS

VI. The Effect of Salts on the Casein-Sodium Hydroxide and Paracasein-Sodium Hydroxide Equilibria*

ALLEN D. ROBINSON, ROSS AIKEN GORTNER AND LEROY S. PALMER**

The nature of the reaction of acids and bases with proteins has been studied by numerous investigators. Conflicting conclusions have been drawn from their work concerning the relative importance of colloidal and chemical forces in these reactions. Gortner¹ sums up the present attitude toward the problem in a statement that there are three schools of thought: One holds to the view that acid- and base-binding by proteins may be explained in terms of strictly chemical forces, another believes that surface energies are involved and a third group maintains that both colloidal and chemical forces play a part. Hoffman and Gortner² favor this view. Their work indicates a chemical type of combination between hydrogen ion concentrations of pH 2.5 and pH 10.5. Above or below the limits of this range their evidence indicates an adsorption type of combination.

Adequate reviews of the work in this field have been given by Robertson,³ Loeb,⁴ Hoffman and Gortner,² Cohn,⁵ and Gortner.¹ More recent contributions are those of Bancroft and Barnett.⁶

Our attention is called at the outset to the number of different methods which have been used to measure the extent of acid- or base-binding by proteins. It is obvious that no single method can of itself tell whether such binding is chemical or colloidal in nature. Such an inference can be made only after giving consideration to the amounts bound under the different sets of conditions. The relatively large number of methods employed over a short span of years is in itself evidence that the problem is far from a complete solution.

Because it was deemed impracticable to separate a protein "salt" from solution in sufficient purity for analysis, as was attempted by Van Slyke and Hart⁷ with "calcium caseinate" and Spiro and Pemsel⁸ with "sodium caseinate," due to alteration in the "salt" during coagulation, investigators have had recourse to indirect methods whereby a measurement of the amount of acid or alkali bound by a protein could be effected. The protein is treated with acid or base in the quantities and under the conditions determined by the experimenter; and the concentration of acid or alkali remaining "unbound" is determined by one of several methods. F. A. Hoffman⁹ measured the catalytic

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effect of the unbound ions on hydrolysis reactions, Sjöqvist¹⁰ determined the change in electrical conductivity, while Bugarszky and Liebermann¹¹ studied the freezing point depression and made potentiometric measurements of the unbound acid or alkali.

The potentiometric method has been deemed the most reliable and has been employed by most subsequent workers. In such a determination it has been generally assumed that the magnitude of the measurement is in no way influenced by the presence of the protein "salt." In other words, the same amount of unbound acid or base in the same volume of aqueous solution should give exactly the same potentiometric reading. This assumption is of doubtful accuracy. A really satisfactory measurement would be one that would not be interfered with by other substances in solution, or would be one to which corrections could be applied for the effect of the other substances which are present.

It has been definitely shown that the alkali bound by protein increases with rising pH and that the acid bound increases with decreasing pH. Gortner¹ points out that this dependence on pH of the amount of reaction occurring suggests that forces of adsorption are involved in the reaction. But Robertson³ states that this is no proof that proteins do not obey the law of constant combining proportions, and points out in defense of his claim that the same change occurs among complex and double salts and the salts of polybasic acids or polyacid bases in the domain of inorganic chemistry. We are asked to visualize a molecule with many acid groups, only part of which ionize in lower concentrations of alkali, but more of which ionize in higher concentrations. Accordingly we have a greater amount of alkali-binding in these higher concentrations because there are more acid groups in a reactive state. A similar explanation is offered for the effect of a lowered pH on the acid-binding of proteins. Loeb⁴ emphasizes that at the same pH a protein will bind equivalent amounts of the different acids or alkalis. One might expect that at an extremely high or low pH, where all the acid or basic groups are ionized, the amount of alkali or acid bound would approach a constant value. Such is not the case. If we are to accept the explanations of Robertson and Loeb, we must consider each protein molecule as having an indefinite number of potential acidic or basic groups differing almost insensibly from each other in their dissociation constants.

Attempts have been made to correlate the binding with the chemical composition of the protein. Greenberg and Schmidt,¹² using Hitchcock's¹³ data, have shown that the amount of acid bound by gelatin is essentially equal to the sum of the free amino nitrogen plus the amino group of arginine. Cohn and Berggren¹⁴ calculate that the casein molecule contains from nineteen to twenty-eight free acid groups, and that casein combines with no more base than is required to neutralize them. Cohn⁵ points out that the more diamino acids a protein contains the more acid it will bind, whereas the more dibasic acids it contains the more alkali it will bind. All this is suggestive of chemical combination, but it does not provide definite proof that adsorption does not play a rôle. Furthermore these investigators worked within a rela-

tively narrow range of pH. With alterations in the systems decided changes in the amounts of acid or base bound might be revealed.

Evidence in favor of an adsorption reaction is seen in the relation between the amounts of alkali or acid bound as related to the original concentration. When graphed such data yield what appears to be an adsorption curve. This has been shown by Tolman and Stearn¹⁵ using fibrin and hydrochloric acid, Herzog and Adler¹⁶ using hide powder, Procter¹⁷ using gelatin, Tolman and Bracewell¹⁸ using fibrin and alkalis, and Izaguirre¹⁹ using the data of Lloyd and Mays²⁰ on hydrochloric acid and gelatin. Weber²¹ did not find this to be true for fibrin and acids.

Van Slyke and Hart⁷ and Van Slyke and Van Slyke²² pointed out that casein binds more acid at lower temperatures than at higher ones. That is, the binding has a negative temperature coefficient. This is not typical of chemical reactions, but is typical of adsorption. The data of Fischer and Hooker²³ with casein reveal the same fact. Weber did not find the reaction between fibrin and hydrochloric acid to have a negative temperature coefficient. Hoffman and Gortner² found a marked negative temperature coefficient of the acid- or alkali-binding at the higher concentrations of acid and alkali than are represented by pH 2.5 and pH 10.5. Within this range the amount of binding was influenced by the chemical composition of the protein; outside the range all proteins showed the same binding capacity, irrespective of their chemical composition. Indeed, when the original concentration was 0.500 normal "there is more alkali bound . . . than can be accounted for by chemical combination assuming that there is an available carboxyl group for each nitrogen atom, an assumption far in excess of possibility." This would mean that within the range pH 2.5 — pH 10.5 the acid and alkali added are neutralized by the amino and carboxyl groups. At pH 2.5 or 10.5 all of these have reacted, and any further reaction must be due to adsorption on the protein micelles. Thomas and Mayer²⁴ found that if acid were added to gelatin the interferometer readings increased in a straight line ratio until a "stoichiometric" point was reached at which the rate of increase became larger but remained a straight line function. This might be interpreted as confirmatory evidence for the theory of Hoffman and Gortner.

Bancroft and Barnett⁵ have made phase rule studies of the proteins. Known amounts of gaseous ammonia or hydrogen chloride were added to dry proteins and the partial pressure of the gas at equilibrium was measured. The pressure-concentration curves for these gases with solid acids or bases showed clearly whether or not definite chemical compounds were formed. A stoichiometric reaction was shown by the appearance of a flat in the curve during which time the solid acid or base was reacting with the gas to form a chemical compound. When applied to proteins it appeared that casein, arachin, zein, fibrin and gliadin adsorb ammonia readily with no evidence of the formation of any chemical compound. Casein, arachin, fibrin, gliadin and edestin did form definite compounds with hydrogen chloride. Zein did not form a chemical compound with hydrogen chloride. The graphs for those

proteins which did form definite chemical compounds indicate that they subsequently adsorb more gas than was necessary for the formation of initial chemical compounds.

The Problem

A new method of attack in the problem of acid and alkali binding is suggested by the work of Kolthoff and Bosch²⁵ on the influence of neutral salts on acid-base equilibria. By determining potentiometrically the pH of successive dilutions of equimolar mixtures of a weak acid and one of its salts they were able to calculate the dissociation constant of the acid, using the Debye-Hückel equation. On the addition of neutral salts to one of the dilutions, changes in pH were noted which were shown to be due to an increase in the activity coefficient of the undissociated acid. The application of this method to protein study is based on the hypothesis that a protein is a weak acid. However the calculations of Kolthoff and Bosch involved the degree of basicity of the acid, its molecular weight and its average ionic size. None of these values are known with any degree of certainty for proteins. So the thermodynamic study as applied to weak acids presents difficulties when applied to proteins. It should be possible however to make similar investigations using a protein as a weak acid, and to judge from the observations recorded whether it behaves as a true electrolyte, or whether it reacts in a manner that can be explained only on the assumption that colloidal behavior is involved.

Both casein and paracasein were chosen for this investigation since we desired to ascertain whether a study of this kind would reveal any deep-seated difference in the chemical nature of the two proteins. Doubts that there is any such difference had already been expressed by Richardson and Palmer.²⁶

Experimental

Reagents.—Paracasein was prepared from skimmed milk according to the method of Van Slyke and Baker²⁷ and Van Slyke²⁸ for casein. Previous to the addition of acid the calcium was precipitated by the addition²⁹ of 0.5 cc. saturated potassium oxalate for every 100 cc. of milk and the precipitate removed by supercentrifuging. The milk was heated to 40°C. and rennet was added. The milk was kept at this temperature for a length of time determined by the time required for the formation of a firm curd when rennet in the same concentration was added to some of the milk from which the calcium had not been removed. Precipitation with acid and solution in alkali for purification then followed the procedure of Van Slyke and Baker.

The protein so prepared analyzed as follows: 5.88% moisture, 0.072% ash, 14.80% nitrogen, 0.863% phosphorus, and 0.621% sulfur. The composition on a moisture-free basis was: ash 0.076%, nitrogen 15.73%, phosphorus 0.91%, sulfur 0.66%. This agrees well with analyses of casein and paracasein reported by Bosworth,³⁰ Geake,³¹ Hammarsten,³² Lehman and Hempel,³³ and Van Slyke and Bosworth.³⁴

Other protein preparations used included one of paracasein used by Richardson and Palmer²⁶ with an ash content of 0.04%. A sample of casein used by

Hoffman and Gortner² was also available. It had an ash content of 0.34%, most of which was porcelain dust derived from grinding the material in a porcelain ball mill. A sample of isoelectric gelatin, having an ash content of 0.13%, was also used.

Pure alanine was used for comparative purposes. The neutral inorganic salts were of "analytical" grade and were ground to a powder, dried for five or six hours at 100°C. and kept in a desiccator. Their aqueous solutions were tested for neutrality with indicators. Only the potassium iodide was not as pure as desired, apparently containing traces of potassium carbonate. The sodium hydroxide solutions used were prepared carbonate-free. Freshly redistilled water collected so as to be free from carbon dioxide was always used.

Apparatus and Methods.—The amount of alkali bound by the protein was determined potentiometrically and is expressed as gram equivalents bound per gram of protein. Measurements were made with a L. and N. Type K potentiometer, using a high resistance galvanometer, readings being made to a tenth of a millivolt. Bailey electrodes and a normal calomel half-cell were used. Appropriate corrections were made for any determinations which were run at temperatures other than 25.0°. All potentiometric readings were calculated to pH values, taking into account appropriate temperature corrections. The values for K_w were likewise corrected for temperature variations, a value of 0.2828 at 25° being used for the value of the calomel cell. The set-up was tested by the use of sodium hydroxide-succinic acid buffers. A series of these is reproduced in Table II as indicative of what may be expected in a system where only chemical combination is taking place.

The protein was made up in 50 cc. volumes of the required degree of alkalinity and salt concentration. Where large enough concentrations of protein were being used, these were weighed into 100 cc. Erlenmeyer flasks, and 0.1 normal carbonate-free base, aliquots of the salt solution, and conductivity water were added to bring the final volume to 50 cc. When the concentration of protein desired was too small to permit of direct weighing without introducing large errors, a stock solution was made in sodium hydroxide of a suitable concentration and aliquots were taken to be diluted subsequently to the desired volume. Stock salt solutions of 1.0, 0.1, 0.01, and 0.001 normality were prepared. When extremely dilute solutions of protein were required, a volume of 300 cc. was used.

The protein dissolved rather readily in solutions at pH 9.0 or 12.0. Difficulty was experienced in securing solution of the protein at a pH near the neutral point. For this work a stock solution of protein in weak alkali was prepared and shaken in a mechanical shaker for twenty-four hours. The final pH of this solution was less than 7.0. In all experiments where the pH of the system exceeded 7.0, the E.M.F. readings were always made within ten hours after the protein was wetted with alkali. According to Cohn and Berggren¹⁴ no appreciable amount of caseose is split off from casein in that time.

Calculations of the amount of alkali bound were made according to the equations of Cohn and Berggren:¹⁴

$$\text{pH} + \text{pOH} = \text{Log } (1/K_w)$$

$$\frac{(\text{OH}^-)}{(\text{NaOH})} = \gamma$$

$$\text{pOH}^- = \log [1/(\text{NaOH})\gamma] = \text{pNaOH} + \text{p}\gamma$$

$$\text{or } \text{pNaOH} = \text{pOH} - \text{p}\gamma.$$

and since $\text{pNaOH} = \log 1/(\text{NaOH})$ the concentration of the uncombined NaOH is readily calculated. The pH was determined from potentiometric measurements. $\log 1/K_w$, the solubility product of water was obtained from Clark's³⁵ tables. Values for $\text{p}\gamma$ were taken from Lewis and Randall,³⁶ using the average values given for γ for Na^+ and OH^- , and obtaining certain values by interpolation from the plotted curves. A table of such values is reproduced by Gortner.¹ From pNaOH the concentration of free sodium hydroxide can be obtained. This subtracted from the original concentration gives the amount "bound" by the protein present.

Certain assumptions are necessary in employing this method of calculation, and we are employing the same assumptions which were made by Cohn and Berggren,¹⁴ in order that our data may be directly compared with theirs. The values for γ were determined from electromotive force measurements in which the activity of the sodium hydroxide was affected by sodium chloride present. In our investigations protein "salts" were present. We therefore assume* for purposes of calculation (1) that the protein and sodium hydroxide react in stoichiometric proportions, (2) that the so-formed protein salt is completely dissociated, (3) γNa^+ of $\text{Na}^+ + \text{proteinate}^- = \gamma\text{Na}^+$ of $\text{Na}^+ + \text{Cl}^-$, (4) therefore, $\gamma \text{proteinate}^- = \gamma\text{Cl}^-$, (5) there is no adsorption of Na^+ or of NaOH on the micelles, and no effect of the ionic micelles on the γ of Na^+ .

In previous investigations^{2,37} it was assumed that the magnitude of the measurement was in no way influenced by the presence of the protein "salt." We now "assume" that the magnitude of its effect is the same as that of the sodium chloride in the concentration in which it was present in the measurements of the value of γ . A comparison of this method of calculation with that of Palmer and Richardson³⁷ and Hoffman and Gortner² using their data shows that the two methods agree closely in the lower ranges of alkali concentration, but differ in the higher ranges. At first this difference shows itself in the present calculations giving a slightly *lower* binding capacity figure, but as the alkali concentration is increased still more the lower values are given by the method of calculation used by Hoffman and Gortner and Palmer and Richardson. We cannot draw hard and fast conclusions from these observations save that differences are noted, particularly at higher

* In order that there may be no misunderstanding it is emphasized that these assumptions are made "for purposes of calculation" and for comparison with Cohn's data. I personally believe that no one of these assumptions is strictly correct. R. A. Gortner.

concentrations of alkali. Opinions may well differ as to which method of calculation is the more nearly correct. Both present obvious inadequacies.

The Effect of pH on the Alkali-binding Capacity of Casein and Paracasein.—It was desired to determine how the amount of alkali bound per gram of paracasein varied with the pH of the equilibrium mixture. Accordingly solutions were prepared in which the concentrations of protein and sodium hydroxide were varied so as to give a series covering a fairly wide range of alkalinity. Measurements and calculations were made as described. The results are recorded in Table I. Data on casein are included for comparison.

Similar determinations were made of the binding of sodium hydroxide by succinic acid. In Table II these results are detailed. The object of these series of measurements was to afford an opportunity to compare the binding by the proteins with the binding by an acid of known constitution, it being known in the latter case that the binding was strictly stoichiometrical.

Two things of significance are noted immediately. In the first place, the amount of alkali bound by succinic acid is essentially a constant. That is, throughout a wide range of hydroxyl ion concentration, succinic acid reacts in the same proportion with sodium hydroxide. This is to be expected as

TABLE I

Comparison of the Alkali-binding Capacity of Casein and Paracasein at Various Degrees of Alkalinity

Sodium Hydroxide	Protein	Casein*		Paracasein*	
		Equilibrium pH	Equivalents of Alkali bound per gm. Protein $\times 10^5$	Equilibrium pH	Equivalents of Alkali bound per gm. Protein $\times 10^5$
Normality	gms. per liter				
0.001	1.0			8.833	99.15
0.006	6.0			9.397	99.44
0.020	10.0	11.230	169.0	11.213	174.68
0.040	20.0	11.411	180.9	11.371	181.89
0.060	30.0	11.487	184.5	11.413	185.8
0.050	20.0	11.863	195.3	11.863	193.0
0.075	30.0	12.003	198.4	11.959	201.4
0.100	40.0	12.083	202.5	12.056	203.4
0.060	20.0	12.118	200.5	12.091	198.6
0.040	10.0	12.125	202.8	12.102	205.1
0.050	10.0	12.289	208.3	12.260	204.5
0.075	20.0	12.335	208.6	12.325	206.0
0.100	30.0	12.369	210.9	12.356	209.6
0.060	10.0	12.407	212.7	12.393	209.7
0.075	10.0	12.531	227.6	12.503	219.7
0.100	20.0	12.536	230.2	12.544	213.6
0.100	10.0	12.667	253.6	12.669	236.7

* Detns. by A. D. R. (1929).

it is conceded that the reaction is strictly stoichiometrical. The amount of alkali bound by the proteins, however, *increases with increasing alkalinity of solution*. This is characteristic of the behavior of proteins. As pointed out previously it has been explained both on the assumption that colloidal forces are entering into the reaction, and that there is an increase in the number of acid groups available for chemical reaction.

The second fact to be noted in our data is that, under similar conditions of concentration and pH, casein and paracasein are very similar in their base-binding capacity. This is contrary to the generally accepted view. In fact the essential difference between the two proteins has always been stated to be the difference in their base-binding capacity. Yet two different workers,

TABLE II

The Alkali-binding Capacity of Succinic Acid at Various Degrees of Alkalinity, Temperature 25°

(Series A and Series B determined by different individuals—R.A.G. and A.D.R.—a year apart and using different solutions and different potentiometric equipment)

	Sodium Hydroxide	Succinic Acid per Liter*	Equilibrium pH	Equivalents of Alkali bound per gram of Succinic Acid** × 10 ⁶
	Normality	Grams		
Series A	0.020	1.1804	7.195	169.43
	0.040	2.3608	8.189	169.42
	0.050	2.3608	11.816	170.25
	0.075	3.5412	12.034	164.88
	0.100	4.7216	12.066	173.12
	0.040	1.1804	12.290	170.41
	0.050	1.1804	12.295	173.59
	0.075	2.3608	12.347	172.65
	0.100	3.5412	12.394	172.54
	0.100	2.3608	12.537	172.14
	0.100	1.1804	12.670	172.65
Series B	0.040	2.3608	10.166	168.51
	0.050	2.3608	11.810	167.38
	0.075	3.5412	12.021	166.21
	0.100	4.7216	12.059	173.69
	0.040	1.1804	12.115	175.53
	0.050	1.1804	12.295	173.59
	0.075	2.3608	12.347	172.65
	0.100	3.5412	12.407	173.86
	0.100	2.3608	12.557	183.70

* These quantities of succinic acid were chosen so that the "alkali bound" would be in the same range as that "bound" in the casein-paracasein series.

** Theory 169.43×10^{-6}

(R. A. G. and A. D. R.), working a year apart, but working in a parallel manner, secure almost identical values for the two proteins. We shall have occasion to refer to this later.

The Effect of Neutral Salts on the Amount of Alkali bound by Casein and Paracasein.—The main object of this study was to test the effect of the addition of various quantities of neutral salts to the protein sodium hydroxide systems. Measurements were made at four varying ranges on the pH scale, the amounts of protein and base being selected so as to obtain this degree of acidity or alkalinity. The salts used with both proteins were potassium chloride, potassium bromide, and potassium iodide. Some data are reported for the casein—NaOH systems where sodium chloride and lithium chloride were used. Rather unsatisfactory results were obtained with the potassium iodide experiments, due probably to the small amount of potassium carbonate contained in the supposedly pure salt. Therefore where figures on potassium iodide are given, it should be recognized that they are recorded merely for purposes of comparison with the effects of the other salts.

The systems were prepared by diluting a sodium hydroxide-paracasein solution with the proper amount of water and stock solutions of neutral salts so as to bring the final solution to the proper concentration. In this manner values were obtained at about pH 12, pH 9, pH 6, and pH 5.

The data for the salt effect at the highest pH are given in Table III. Data on the effect of dilution of the protein-base system of the same relative concentration as used in the "salt effect" studies are included, it being deemed desirable to have this available for purposes of calculation. Table III includes as well dilution data for a casein-sodium hydroxide system of the same concentration and the effect of potassium chloride and sodium chloride on such a casein system.

Certain features appear outstanding in these data. The effect of the three salts on the paracasein-sodium hydroxide system at this range of pH is practically identical. It is true that potassium iodide seems to exert a slightly different magnitude of effect than the others, but this is due probably to impurities in the salt as pointed out above. There does not appear to be a significant lyotropic series for the anions. Whether any significance should be attached to the fact that when the data are plotted the curves resemble those of the adsorption type, we shall leave until later to decide.

It would appear then that either there are unjustifiable assumptions in the method of calculation which was employed, or else that in some manner the presence of a neutral salt increases the base-combining capacity of a protein. Different neutral salts with a common univalent cation and different monovalent anions exert essentially equal effects in increasing this capacity. At a pH of approximately 12 it becomes noticeable in salt solutions as dilute as 0.0025 normal. Salt solutions weaker than this exert no appreciable

TABLE III

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 11 to pH 12.5

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein			Casein		
			pH	Equivalents* of Alkali bound per gm. Protein $\times 10^5$	Equivalents* of Alkali bound per gm. Protein $\times 10^5$	pH	Temperature °C.	Equivalents** of Alkali bound per gm. Protein $\times 10^5$
None	20	0.100	—	—	—	—	25	12.579
"	15	0.075	12.407	227.5	213.0	12.429	25	12.465
"	12	0.060	12.330	218.3	204.7	12.351	25	12.386
"	10	0.050	12.282	204.5	200.8	12.300	25	12.313
"	8	0.040	12.163	200.0	205.6	12.184	25	12.230
"	4	0.020	11.875	209.2	190.0	11.920	25	11.952
"	2	0.010	11.553	232.1	188.5	11.619	25	11.682
"	1	0.005	11.345	179.0	170.4	11.391	25	11.418
"	0.3333	0.00167	10.901	168.1	136.0	10.944	25	10.979
0.5000 N KCl	10	0.05	12.176	256.5	241.2	12.184	—	—
0.2500 "	10	0.05	12.209	247.4	234.8	12.195	—	—
0.1000 "	10	0.05	12.203	240.9	228.0	12.189	—	—
0.0500 "	10	0.05	12.231	234.3	221.1	12.200	—	—
0.0250 "	10	0.05	12.201	231.2	216.2	12.227	—	—
0.0100 "	10	0.05	12.212	224.3	215.6	12.208	—	—
0.0050 "	10	0.05	12.214	221.5	212.9	12.195	—	—
0.0025 "	10	0.05	12.278	203.9	211.6	12.197	—	—
0.0010 "	10	0.05	12.277	204.2	205.2	12.224	—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE III (continued)
Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 11 to pH 12.5

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein			Casein		
			pH	Equivalents* of Alkali bound per gm. Protein $\times 10^4$	pH	Equivalents* of Alkali bound per gm. Protein $\times 10^4$	Temperature	Equivalents** of Alkali bound per gm. Protein $\times 10^4$
0.5000 N KBr	10	0.05	12.126	264.8	—	—	—	—
0.2500 " "	10	0.05	12.154	249.1	—	—	—	—
0.1000 " "	10	0.05	12.162	244.5	—	—	—	—
0.0500 " "	10	0.05	12.177	236.0	—	—	—	—
0.0250 " "	10	0.05	12.219	219.5	—	—	—	—
0.0100 " "	10	0.05	12.224	216.2	—	—	—	—
0.0050 " "	10	0.05	12.235	208.9	—	—	—	—
0.0025 " "	10	0.05	12.135	217.9	—	—	—	—
0.0010 " "	10	0.05	12.244	204.5	—	—	—	—
0.5000 N KI	10	0.05	12.092	282.5	—	—	—	—
0.2500 " "	10	0.05	12.133	261.0	—	—	—	—
0.1000 " "	10	0.05	12.184	230.8	—	—	—	—
0.0500 " "	10	0.05	12.200	220.7	—	—	—	—
0.0250 " "	10	0.05	12.212	213.1	—	—	—	—
0.0100 " "	10	0.05	12.215	210.9	—	—	—	—
0.0050 " "	10	0.05	12.235	197.3	—	—	—	—
0.0025 " "	10	0.05	12.241	205.3	—	—	—	—
0.0010 " "	10	0.05	12.228	202.5	—	—	—	—
0.5000 N NaCl	10	0.05	—	—	—	—	25	222.2
0.2500 " "	10	0.05	—	—	—	—	25	211.6
0.1000 " "	10	0.05	—	—	—	—	25	200.8
0.0500 " "	10	0.05	—	—	—	—	25	199.4
0.0250 " "	10	0.05	—	—	—	—	25	197.3
0.0100 " "	10	0.05	—	—	—	—	25	193.1

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE IV
Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality	Concentration of Protein gm. per liter	Sodium Hydroxide Normality	Paracasein*		Casein		Equivalents** of Alkali bound per gm. Protein $\times 10^5$
			pH	Equivalents of Alkali bound per gm. Protein $\times 10^5$	pH	Temperature $^{\circ}\text{C}$.	
None	20.0	0.02	—	—	—	25	99.78
"	10.0	0.0100	—	—	—	25	99.44
"	7.5	0.0075	9.370	99.57	9.578	—	—
"	6.0	0.0060	9.397	99.44	9.574	—	—
"	5.0	0.0050	9.349	99.40	9.582	25	99.86
"	4.0	0.0040	9.298	99.34	9.550	—	—
"	2.0	0.0020	9.014	99.32	9.460	—	—
"	1.0	0.0010	8.833	99.15	9.300	—	—
"	0.5	0.0005	8.487	99.21	8.982	28	97.74
"	0.167	0.000167	7.653	99.67	8.183	29	98.50
0.500	10	0.010	—	—	—	25	99.65
0.500	5	0.005	8.723	99.85	9.206	25	99.37
0.250	10	0.010	—	—	—	25	99.67
0.250	5	0.005	8.766	99.83	9.223	25	99.41
0.100	10	—	—	—	—	25	99.65
0.100	5	0.005	8.839	99.80	9.256	25	99.36
0.0500	5	0.005	8.927	99.75	9.309	29	99.52
0.0250	5	0.005	9.016	99.70	9.396	29	99.45
0.0100	5	0.005	9.123	99.62	9.476	29	99.35
0.0050	5	0.005	9.176	99.56	9.532	—	—
0.00250	5	0.005	9.272	99.46	9.555	—	—
0.00100	5	0.005	9.250	99.44	9.571	—	—
0.00050	5	0.005	9.286	99.41	—	—	—
0.00025	5	0.005	9.275	99.41	—	—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE IV (continued)
Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein*		Casein		
			pH	Equivalents of Alkali bound per gm. Protein $\times 10^4$	pH	Equivalents* of Alkali bound per gm. Protein $\times 10^4$	Equivalents** of Alkali bound per gm. Protein $\times 10^4$
0.500 N KBr	5	0.005	8.653	99.88	—	—	99.39
0.250 " "	5	0.005	8.762	99.85	—	—	99.41
0.100 " "	5	0.005	8.820	99.82	—	—	99.40
0.050 " "	5	0.005	8.973	99.75	—	—	—
0.025 " "	5	0.005	9.049	99.70	—	—	—
0.010 " "	5	0.005	9.133	99.64	—	—	—
0.0050 " "	5	0.005	9.218	99.54	—	—	—
0.0025 " "	5	0.005	9.264	99.51	—	—	—
0.0010 " "	5	0.005	9.311	99.43	—	—	—
0.0005 " "	5	0.005	9.279	99.40	—	—	—
0.500 N KI	5	0.005	8.972	99.84	—	—	99.33
0.250 " "	5	0.005	8.800	99.83	—	—	99.45
0.100 " "	5	0.005	8.825	99.82	—	—	99.39
0.050 " "	5	0.005	8.912	99.73	—	—	—
0.025 " "	5	0.005	9.019	99.67	—	—	—
0.010 " "	5	0.005	9.162	99.62	—	—	—
0.005 " "	5	0.005	9.227	99.55	—	—	—
0.0025 " "	5	0.005	9.206	99.49	—	—	—
0.0010 " "	5	0.005	9.267	99.42	—	—	—
0.0005 " "	5	0.005	9.276	99.41	—	—	—

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

TABLE IV (continued)

Dilution and Salt Effect Data for Casein- and Paracasein-Sodium Hydroxide Systems at pH 8 to 9.6

Salt Normality	Concentration of Protein	Sodium Hydroxide	Paracasein*			Casein		
			pH	Equivalents of Alkali bound per gm. Protein $\times 10^5$	pH	Equivalents* of Alkali bound per gm. Protein $\times 10^5$	Temperature	pH
0.500 N NaCl	10	0.010	—	—	—	—	25	9.224
0.500 "	5	0.005	—	—	—	—	25	9.090
0.250 "	10	0.010	—	—	—	—	25	9.260
0.250 "	5	0.005	—	—	—	—	25	9.159
0.100 "	10	0.010	—	—	—	—	25	9.324
0.100 "	5	0.005	—	—	—	—	25	9.211
0.050 "	5	0.005	—	—	—	—	29	9.045
0.025 "	5	0.005	—	—	—	—	29	9.144
0.010 "	5	0.005	—	—	—	—	29	9.236
0.500 N LiCl	10	0.010	—	—	—	—	25	9.195
0.500 "	5	0.005	—	—	—	—	25	9.163
0.250 "	10	0.010	—	—	—	—	25	9.234
0.250 "	5	0.005	—	—	—	—	25	9.171
0.100 "	10	0.010	—	—	—	—	25	9.317
0.100 "	5	0.005	—	—	—	—	25	9.207

* Detns. by A. D. R. (1929).

** Detns. by R. A. G. (1928).

effect on the base-binding capacity of paracasein. From our study we would designate 0.001 normality to be the "fading out" point of the salt effect.*

Table IV shows the salt effect on the paracasein-sodium hydroxide and casein-sodium hydroxide systems at approximately pH 9. It includes dilution data as well. Here we have results very similar to those observed at the higher pH. The addition of neutral salts increases the base-binding capacity of paracasein, and the order of the increase appears superficially to resemble the typical adsorption curve. As before, the three salts seem to exert equal effects. The fading out point of the salt effect however is at a normality of 0.00025 to 0.0005 as compared with 0.001 at the higher pH. Salt concentrations which appear to have no effect on paracasein at pH 12 will cause it to bind more alkali at pH 9.**

In general the casein results agree with those for the paracasein systems. The actual figures are not the same, though nearly so. The amount of alkali bound by the paracasein is in general slightly greater than that bound by casein. While the fading out point was not determined for casein-sodium hydroxide systems, it would appear to be similar to that for paracasein.

Table V gives the dilution and salt effect data for casein and paracasein systems at a pH of approximately 6. It will be noted that whereas in previous dilution studies, dilution *lowered* the pH of a solution, in this case it *raised* it. This is due of course to the fact that while we have alkali present, it is not present in sufficient quantity to overcome the acidity of the protein. We are merely making an acid solution less acid by dilution.

The salt effect is similar to that in the previous series. The fading out point is reached at a salt concentration of 0.0001 normality, lower than in any of the previous studies. That is, the lower the pH, or perhaps the more nearly "neutral" the solution is, the more effect do small quantities of neutral salts produce.

For purposes of comparison similar studies were made on an amino acid-sodium hydroxide system, alanine being the amino acid used. The dilution and salt effect data are reproduced in Table VI. Measurements were also made of the salt effect of a neutral salt containing a divalent cation, calcium chloride. It was impossible to use this salt in paracasein studies, due to the formation of a curd of "calcium paracaseinate." Like the proteins, alanine binds more alkali in the presence of a neutral salt. The calcium chloride

* In most of the data which are reported for casein, the salt solutions were not sufficiently dilute to prevent a shift in the pH of the casein-NaOH system. A distinct "salt effect" persists at a salt concentration of 0.01 N and this "salt effect" fades out only as we approach 0.0010 N salt concentration. There is, therefore a greater "salt effect" in these casein-NaOH systems than Kolthoff and Bosch²⁸ found in their acid-base equilibria studies. However, the data which we do present is adequate to demonstrate that the paracasein-NaOH system is essentially identical in its behavior in this respect to the casein-NaOH system.

** Admittedly the excess "binding" due to the presence of the salt appears to be very small numerically; thus the values are 99.85×10^{-5} equivalents in the presence of 0.5 N KCl and 98.54×10^{-5} equivalents in the salt-free system. These extremes, however, represent a range in equilibrium pH values of 8.723 and 9.349 respectively, and accordingly represent readily measurable differences. There is no question but that these systems show a pronounced "salt effect."

TABLE V
Dilution and Salt Effect Data for Casein and Paracasein-Sodium Hydroxide Systems at pH 6 to 7

Salt Normality	Concen- tration of Protein	Sodium Hydroxide Normality	Paracasein*		Temper- ature °C.	Casein**	
			pH	Equivalents of Alkali bound per gm. × 10 ⁵		pH	Equivalents of Alkali bound per gm. × 10 ⁵
None	10.0	0.0050	—	—	27	6.657	49.9993
"	7.5	0.00375	6.601	49.9993	—	—	—
"	6.0	0.00300	6.622	49.9991	—	—	—
"	5.0	0.00250	6.630	49.9988	27	6.703	49.9984
"	4.0	0.00200	6.658	49.9984	—	—	—
"	2.0	0.00100	6.713	49.9965	—	—	—
"	1.0	0.00050	6.768	49.9925	—	—	—
"	0.5	0.00025	6.743	49.9858	27	6.836	49.9793
"	0.167	0.0000833	6.825	49.8492	27	7.235	49.8415
0.50000 N KCl	5	0.0025	5.865	49.99981	27	6.080	49.99957
0.25000 "	5	0.0025	5.930	49.99978	27	6.131	49.99948
0.10000 "	5	0.0025	6.064	49.99970	27	6.238	49.99935
0.05000 "	5	0.0025	6.166	49.99961	—	—	—
0.02500 "	5	0.0025	6.273	49.99951	—	—	—
0.01000 "	5	0.0025	6.399	49.99931	—	—	—
0.00500 "	5	0.0025	6.479	49.99917	—	—	—
0.00250 "	5	0.0025	6.540	49.99905	—	—	—
0.00100 "	5	0.0025	6.581	49.99896	—	—	—
0.00050 "	5	0.0025	6.562	49.99887	—	—	—
0.00025 "	5	0.0025	6.571	49.99885	—	—	—
0.00010 "	5	0.0025	6.587	49.99881	—	—	—

* Data of A. D. R. (1929).

** Data of R. A. G. (1928).

TABLE V (continued)
Dilution and Salt Effect Data for Casein and Paracasein-Sodium Hydroxide Systems at pH 6 to 7

Salt Normality	Concen- tration of Protein	Sodium Hydroxide	Paracasein *		Temper- ature	Casein **	
			pH	Equivalents of Alkali $\times 10^5$		pH	Equivalents of Alkali bound per gm. $\times 10^5$
0.50000 N KBr	5	0.0025	5.843	49.99979	—	—	—
0.25000 " "	5	0.0025	5.912	49.99977	—	—	—
0.10000 " "	5	0.0025	6.043	49.99969	—	—	—
0.05000 " "	5	0.0025	6.145	49.99960	—	—	—
0.02500 " "	5	0.0025	6.242	49.99950	—	—	—
0.01000 " "	5	0.0025	6.351	49.99936	—	—	—
0.00500 " "	5	0.0025	6.438	49.99922	—	—	—
0.00250 " "	5	0.0025	6.497	49.99911	—	—	—
0.00100 " "	5	0.0025	6.551	49.99903	—	—	—
0.00050 " "	5	0.0025	6.571	49.99889	—	—	—
0.00025 " "	5	0.0025	6.600	49.99887	—	—	—
0.00010 " "	5	0.0025	6.600	49.99882	—	—	—
0.10000 N KI	5	0.0025	6.038	49.99969	—	—	—
0.05000 " "	5	0.0025	6.146	49.99960	—	—	—
0.02500 " "	5	0.0025	6.234	49.99951	—	—	—
0.01000 " "	5	0.0025	6.369	49.99936	—	—	—
0.00500 " "	5	0.0025	6.442	49.99924	—	—	—
0.00250 " "	5	0.0025	6.513	49.99914	—	—	—
0.500 N NaCl	5	0.0025	—	—	27	6.006	49.9996
0.250 " "	5	0.0025	—	—	27	6.086	49.9995
0.100 " "	5	0.0025	—	—	27	6.220	49.9994
0.500 N LiCl	5	0.0025	—	—	27	6.074	49.9995
0.250 " "	5	0.0025	—	—	27	6.130	49.9995
0.100 " "	5	0.0025	—	—	27	6.208	49.9994

* Data of A. D. R. (1929).

** Data of R. A. G. (1928).

effect exceeded that of potassium chloride. It is probable that the salt of a divalent cation has a greater effect on the alkali-binding capacity of a protein than has the salt of a monovalent cation, both salts having a common anion. It will further be noted that the theoretical equivalents of NaOH were bound only when essentially equivalent amounts of the amino acid and the alkali were present.

TABLE VI

Dilution and Salt Effect Data for Alanine-Sodium Hydroxide System at pH 9.2 to 10

Salt Normality	Alanine Normality	Sodium Hydroxide Normality	pH	Equivalents of Alkali bound per Mole of Alanine* $\times 10^3$
None	0.0200	0.0100	9.775	495.5
"	0.0150	0.0075	9.791	404.2
"	0.0120	0.0060	9.785	491.2
"	0.0100	0.0050	9.767	491.5
"	0.0080	0.0040	9.767	489.5
"	0.0040	0.0020	9.788	480.5
"	0.0020	0.0010	9.747	466.3
"	0.0010	0.0005	9.659	445.3
"	0.0003	0.00016	9.203	439.1
0.5000 N KCl	0.01	0.005	9.670	493.2
0.2500 " "	0.01	0.005	9.677	493.4
0.1000 " "	0.01	0.005	9.699	493.0
0.0500 " "	0.01	0.005	9.703	492.7
0.0250 " "	0.01	0.005	9.721	492.7
0.0100 " "	0.01	0.005	9.750	492.1
0.0050 " "	0.01	0.005	9.767	492.2
0.0025 " "	0.01	0.005	9.763	491.9
0.0010 " "	0.01	0.005	9.763	491.9
0.5000 N CaCl ₂	0.01	0.005	9.376	496.4
0.2500 " "	0.01	0.005	9.496	495.5
0.1000 " "	0.01	0.005	9.571	494.6

* Theory = 449.08×10^{-3} .

Studies were made of the effect of salts on protein-water systems. Any results obtained in these could not be reported in terms of the effect on the alkali-binding capacity of the protein. But increase in base-binding capacity is accompanied by a lowering of the pH of the system. Casein-water, paracasein-water, gelatin-water, and alanine-water systems were treated with varying amounts of potassium chloride and the effect upon the pH of the system determined. These results are recorded in Tables VII and VIII.

TABLE VII

The Effect of KCl on the pH of Protein-in-H₂O Systems

Concentration of Protein in Gm. per liter	KCl	Casein	Paracasein	Gelatin
	Normality	pH	pH	pH
2	0.5000	4.910	4.884	5.070
2	0.2500	4.931	4.917	5.014
2	0.1000	4.986	4.960	5.018
2	0.0500	5.003	4.976	5.088
2	0.0250	5.040	4.984	5.074
2	0.0100	4.959	5.035	4.923
2	0.0050	4.978	5.115	4.926
2	0.0025	4.999	5.180	4.962
2	0.0010		5.217	4.910
2	0.0005			4.955
2	0.0000	5.137	5.356	5.003
40	0.0000	4.738	5.104	
40	0.0100	4.832	4.978	

TABLE VIII

Effect of KCl on the pH of an Alanine-in-H₂O Solution

Conc. Alanine = 0.2 moles per liter

KCl	pH	KCl	pH
Normality		Normality	
0.500	6.635	0.025	6.730
0.250	6.668	0.010	6.710
0.100	6.697	0.000	6.800
0.050	6.721		

The addition of increasing amounts of potassium chloride lowers the pH of the alanine in water solution. This effect is similar to the salt effect on the protein-base system. A similar effect is indicated for the casein-water and paracasein-water systems, though all data are not in harmony with this generalization. Values which do not fall in line with the general trend are due probably to experimental errors of measurement. On repeating these studies a similar series of data was obtained, but with values of slightly different magnitude. It will be observed that the casein and paracasein impart different pH values of the water systems, that for paracasein being the higher. The magnitude of the salt effect seems to be of the same order for both proteins.

It seems impossible to draw any conclusions from the gelatin studies. There is no apparent relationship between salt concentration and direction or magnitude of change in pH.

Discussion

Base-binding Capacity.—The difference in base-binding capacity of casein and paracasein and of succinic acid has already been discussed at some length. The amount of alkali bound by casein and paracasein was found to increase with the equilibrium pH, whereas the amount bound by succinic acid was constant over a wide pH range. This would indicate that other factors than a stoichiometrical combination were acting—possibly an adsorption type of reaction between protein and alkali being added to a stoichiometrical binding. If this were due to increased ionization of the protein as an acid at higher pH values we might reasonably expect to find a point at which the protein ceases to bind larger quantities of alkali. That is, all the carboxyl groups would have reacted, and there would be no further salt formation between the protein and the alkali. From this point on, the amount of alkali bound per gram of protein would be the same, irrespective of the pH of the solution. This constant value was not reached, even though the systems were studied at pH 12.7. It would appear doubtful then if those who believe the reaction to be strictly stoichiometrical are justified in their stand. No amount of hypothetical argument will alter the fact that the curve for the alkali-binding of a protein over a changing pH range does not resemble the one for the alkali-binding of an organic acid of known constitution and which dissolves to form a true solution.

The Dilution Series.—The dilution data for the various systems are of interest. It is impossible to make use of them to calculate dissociation constants, as Kolthoff did, for reasons which have been previously stated. His first step was to determine the pH at infinite dilution, using the Debye-Hückel equation:

$$-\log f_1 = 0.5\sqrt{\mu}$$

where μ is the concentration. The value 0.5 may be employed if we are dealing with a monobasic acid, as acetic acid. For a dibasic acid, 1.5 would be used; for a tribasic one, 2.5; etc. Assuming paracasein does dissociate as an acid, we may let its degree of basicity be equal to $x + 1$. Then the equation would become

$$-\log f_1 = (x + 0.5)\sqrt{\mu}$$

Assuming that the dilutions were carried far enough, then the values for the greater dilutions, substituted in the above equation should yield values from which we might express the pH at infinite dilution in terms of the basicity of paracasein, or

$$\text{pH}^\infty = \text{pH} + (x + 0.5)\sqrt{\mu}$$

Thus from the dilution data for paracasein in Table III,

$$\text{pH}^\infty = 11.553 + (x + 0.5)\sqrt{0.01}$$

$$\text{pH}^\infty = 11.345 + (x + 0.5)\sqrt{0.005}$$

using these as simultaneous equations and solving for x , we find that $x = -7.6$, or the degree of basicity $= -6.6$. Similar calculations from other series of the dilution data yield values for $x + 1$ as follows:

	Paracasein	Casein
Table III	- 6.6	- 7.4
Table IV	-34.1	-31.3
Table V	- 3.7	

In each case, the degree of basicity of the acid (paracasein or casein), has a negative value. This is a necessary consequence since the two terms of the expression for pH^∞ are smaller in one case than in the other. That is, a decreasing pH is accompanied by a decreasing value under the square root sign. These expressions then can be equal only if x is negative. Whereas we might expect more satisfactory results for alanine, we find it responding to our calculations after the manner of the proteins to give a degree of basicity of -8.3 . Alanine is known to be monobasic. It would accordingly appear that this method of calculation cannot be applied to amphoteric electrolytes.

From the dilution data we are led to draw two conclusions. First, our studies do not lend themselves to ready theoretical mathematical interpretation. This may be due to the fact that there is not the constant proportion between the reacting substances that we expect in a strictly stoichiometrical reaction, or it may be due to effects other than stoichiometrical combination. In fact, this lack of definiteness suggests strongly that classical chemical effects are not responsible for the whole of the reaction. It has been pointed out by Randall and his coworkers^{38,39} that thermodynamic method cannot be applied in heterogeneous systems. These observations throw doubt on the question of applying thermodynamic equilibrium calculations to our data.

Secondly, we have seen that the proteins "bind" different amounts of alkali, the amount which is bound depending both upon the concentration of the protein and the concentration of the alkali. This confirms other findings.

The Effect of Salts on the Reaction between Proteins and Sodium Hydroxide.

—The presence of salts, such as KCl, KBr and KI, increase the ability of the protein to "bind" sodium hydroxide and when the equivalents of alkali bound per gram of protein are plotted against the normality of the salt solution, the resulting curves approximate parabolas and indicate that adsorption may be involved in the increase. In order to test this possibility, the logarithms of salt normality were plotted against the logarithms of alkali bound per gram of protein. A representative curve is shown in Fig. 1. In this figure (paracasein-NaOH-KCl at pH 12), it is seen that the curve approximates a straight line, except for extremely small values of salt concentration. Accordingly it would appear that at this pH the increase in the alkali binding is probably due to adsorption.

Paracasein-NaOH-salts at pH 9 and paracasein-NaOH-salts at pH 6 did not yield straight lines, but rather sigmoid curves with a greater curvature

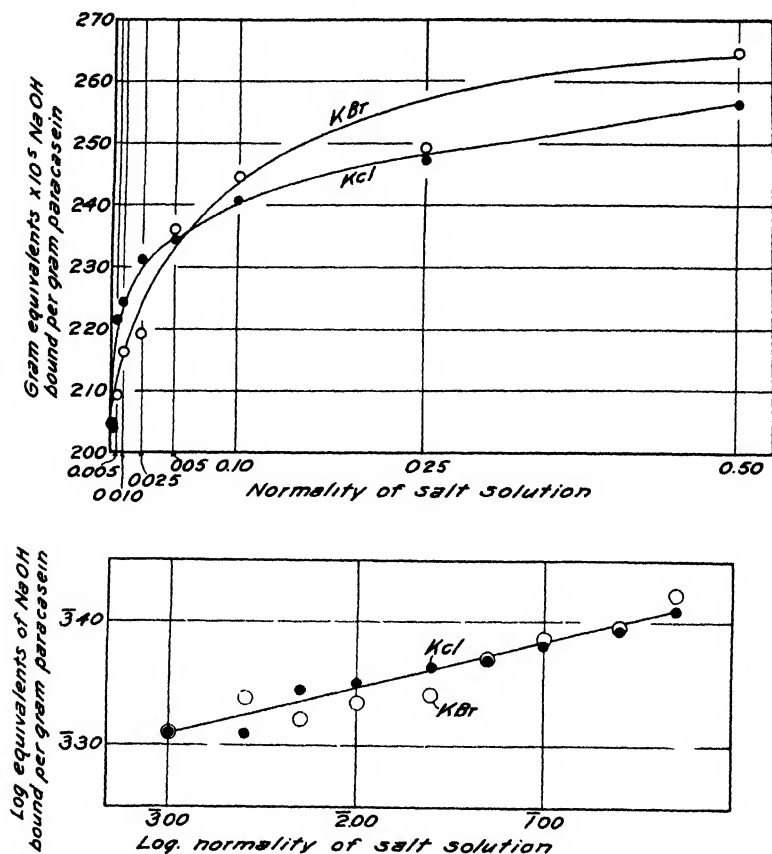


FIG 1

Showing the effect of various concentrations of KCl and KBr on the alkali binding of paracasein at approximately pH 12.

at pH 6 than at pH 9. It would thus appear that there is less of an adsorption effect at pH 6 than at pH 9 and less at pH 9 than at pH 12. We believe that there is certainly some adsorption at pH 9, and possibly some at pH 6.

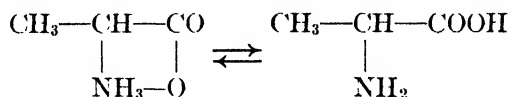
These findings appear to substantiate the findings of Hoffman and Gortner.² Adsorption is primarily concerned in the extra binding at pH 12, while more nearly classical chemical forces were involved at pH 9 and pH 6, more so in the latter than in the former. If the effect of added salts is to increase the activity of the undissociated molecule, as Kolthoff and Bosch found for certain acids, then the above is simple of explanation. The increased activity may result in increased power of adsorption and increased opening up of active groups. In the lower pH ranges where complete stoichiometrical binding has not occurred, there is further increase in the active groups followed by chemical reactions. Above pH 10.5, where the stoichiometrical binding is completed, the increased activity results in adsorption although some adsorption may occur below pH 10.5.

At lower pH values a shift in the equilibrium pH is observed with a lower salt concentration than at a higher pH. Kolthoff and Bosch²⁵ found that the salt effect in relatively simple acid-base systems disappeared at much higher concentrations of salt than those which we have found to show a decided effect in the casein- and paracasein-NaOH systems. Kolthoff,* after reviewing our data, comments on this fact as follows: "The striking effect of small amounts of neutral salts on the pH of the caseinate solutions shows definitely that they do not behave like simple acid-base systems of the classical type."

It should furthermore be emphasized that there is no definite lyotropic series for the anions Cl, Br and I in the "salt effect." Whether there is one for cations we did not determine. It is probable that a divalent cation would produce a greater effect than does a monovalent one.

This "salt effect" in a protein-NaOH system offers a logical explanation for the divergence which Hoffman and Gortner¹⁰ found in a comparison of the "titration curve" and the "back titration curve" of a protein-NaOH-HCl system. They observed that when proteins were electrometrically titrated with sodium hydroxide (or calcium hydroxide) and then the mixture was back-titrated with equivalent amounts of hydrochloric acid, the "back-titration curve" invariably was different from the original titration curve, being shifted toward lower pH values. Due to the presence of the "salt effect" which we have noted, it is a necessary consequence that the second curve did not coincide with the initial one. Accordingly, the interpretation of pH measurements made in protein systems containing even small quantities of neutral inorganic salts is complicated by the concomitant "salt effect."

No explanation is offered for the increased reactivity of alanine with sodium hydroxide in the presence of salts. It can hardly be explained by an increase in the dissociation of alanine or by a shift of the internal salt equilibrium to the right:



Either the assumptions upon which our calculations are based are at fault, or else the amino group is in some unknown manner entering into the reaction. It cannot be through the formation of carbamino salts, since every precaution was taken to avoid the presence of carbon dioxide.

In the tables, data have been reported which were obtained from single preparations of casein and paracasein. That other preparations yield essentially identical data was proven by working with two other preparations of casein which have been used for physico-chemical studies in our laboratories. One of these samples was that used by Richardson and Palmer.²⁶ We also tested their sample of paracasein and secured values which were within experimental error of those which we report.

Therefore, as our contribution to the casein-paracasein problem, we must conclude that technic such as we have used shows little if any difference

* Private communication.

in these two proteins. Both bind approximately the same amounts of sodium hydroxide and both show essentially the same salt effect. If however we compare the dilution data for the two proteins as presented in Table III, we find that somewhat more alkali is bound by paracasein than by casein at similar concentrations of protein and alkali, or at the same pH. This is in harmony with the generally accepted notion of the reaction of the two proteins. Yet it is contrary to the findings presented in Table I. In general the systems reported in Table I were much more concentrated than were those reported in Table III. As a matter of fact only two of the systems had identical concentrations in both series, and the concentration of the system unquestionably affects the amount of base which is "bound" even though the ratio of protein:NaOH may be identical.

Summary and Conclusions

1. The amount of sodium hydroxide "bound" by casein and paracasein increased with the equilibrium pH. This suggests that adsorption may play a part in the reaction.
2. In similar studies succinic acid "bound" a constant amount of sodium hydroxide over an increasing pH range.
3. At pH 12.2 adsorption was probably the factor causing increased combination. At pH 9.0 and pH 6.0, binding by acidic groups appears to largely account for the results obtained.
4. The amount of sodium hydroxide "bound" by casein and paracasein is increased by the presence of potassium chloride, potassium bromide, or potassium iodide.
5. The addition of neutral salts causes a shift in the equilibrium pH of a casein-NaOH or a paracasein-NaOH system toward a lower pH value. This "salt effect" is much more pronounced in these protein-base systems than has been reported to be the case for simpler acid-base systems. Concentrations of neutral salts, as low as 0.001 N in some instances, produced a measurable pH shift.
6. The magnitude of the salt effect is essentially the same for potassium chloride, potassium bromide and potassium iodide. This "salt effect" exhibits no marked lyotropic series for these anions. These protein-NaOH systems are more sensitive to the addition of salts at a pH closer to their isoelectric points than at one further away.
7. This "salt effect" must be taken into consideration in the interpretation of the electrometric titration curves of proteins. If one titrates proteins electrometrically with either acid or alkali and then back-titrates the resulting system, the back-titration curve, due to the salt effect, will not coincide with the original titration curve. If a protein solution contains even small quantities of neutral inorganic salts, the equilibrium pH which is attained on the addition of a definite quantity of acid or alkali will be different from that which would be attained in the absence of the neutral inorganic salts.

8. In the pH ranges studied, and with the methods employed, casein and paracasein react essentially alike. The paracasein, in some instances, appears to bind slightly more alkali than does casein. Both respond in the same manner to the addition of salts.

9. This study affords evidence that a strictly classical thermodynamical treatment of the data of protein systems does not indicate a "maximum binding capacity" of NaOH by either casein or paracasein, such as is a necessary consequence of a stoichiometrical salt-formation, uncomplicated by adsorption reactions. The amount of sodium hydroxide which is bound by either casein or paracasein increases with increasing equilibrium hydrogen ion concentration in spite of attempts to apply assumptions of a strictly stoichiometrical combination to the calculation of the data.

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SOME REMARKS ON THE USE OF THERMOPILES FOR THE ABSOLUTE MEASUREMENT OF RADIANT ENERGY*

BY PHILIP A. LEIGHTON AND WESLEY G. LEIGHTON

Among the instruments which may conveniently be applied to the accurate measurement of radiant energy in absolute terms,** the thermopile, used with a sensitive galvanometer,¹ has come into almost universal use. In photochemistry, for example, almost every value of quantum yields which has yet been published depends, directly or indirectly, upon a calibrated thermopile as the instrument for the determination of the absolute amount of energy involved.

The measurement of relative light intensities, itself a matter demanding the most careful technique, is simple compared to the translation of these measurements into absolute units. During the past eight years, the authors have investigated thirteen thermopiles, involving seven distinct types of construction, with regard to their applicability to absolute energy measurements. Some of the results of these studies have been published in connection with the work for which the thermopiles were used, and descriptions of most of the errors involved, together with precautionary measures, have been published by others, but the statements are so widely scattered through the literature that the knowledge seems to be gained by each new worker largely through experience. It therefore seems worth while to publish in one account a description of the observations which have been made and the precautions which have been found necessary in order to obtain reliable results.

1. Remarks on Design and Construction

Much of the work on the design and construction of line and surface thermopiles suitable for absolute energy measurements has been carried out by W. W. Coblentz,² who gives detailed directions for their construction. The absolute thermopile of Coblentz and Emerson merits more attention than it has received. The construction of line and surface thermopiles has also been described by Johansen,³ Voege,⁴ Moll,⁵ and others.⁶ Single junction thermo-

* Contribution from the Chemistry Laboratories of Stanford University and of Pomona College.

** The term "energy" as here used refers to energy per unit time. We believe this is preferable to the use of the term "intensity" since energy per unit area is usually not considered.

¹ G. S. Forbes: *J. Phys. Chem.*, **32**, 489-90 (1928)

² Coblentz: *Bur. Standards Bull.*, **4**, 391 (1908); **12**, 503 (1916); **9**, 7 (1913); **11**, 131 (1914); *Bur. Standards Sci. Papers*, **17**, 187 (1921); *J. Opt. Soc. America*, **5**, 259 (1921); **7**, 439 (1923).

Coblentz and Emerson: *Bur. Standards Bull.*, **11**, 157 (1914); **12**, 505 (1916).

³ Johansen: *Ann. Physik*, (4) **33**, 517 (1910).

⁴ Voege: *Physik. Z.*, **21**, 288 (1920); **22**, 119 (1921).

⁵ Moll: *Proc. Phys. Soc. London*, **35**, 257 (1923).

⁶ Weigert: "Optische Methoden der Chemie," 295 (1927).

couples of high sensitivity but with small sensitive surface are described by Moll and Burger,⁷ Brackett and McAlister,⁸ and Petit and Nicholson.⁹ A single thermocouple adapted to absolute energy measurements has recently been employed by Beckmann and Dickinson.¹⁰

The majority of these instruments have been designed with cases which may be evacuated. Evacuation is found to increase the sensitivity from two to twelve times over that at atmospheric pressure. In case a vacuum thermocouple or thermopile is used, care must be taken that the pressure is very low (less than 10^{-4} mm.) or that it is constant, since in the pressure range between 10 mm. and 10^{-3} mm. the sensitivity changes rapidly with pressure.⁹ The sensitivity is also a function of the nature of the enclosed gas. Using a surface thermopile, we have found the sensitivity in an atmosphere of hydrogen is less than half of that in air, pressure being atmospheric in both cases, and even at a pressure of 10^{-4} mm., the sensitivity in hydrogen is slightly less than that in air. The question of the position of the slit with respect to the radiation receivers must be considered in the design of vacuum thermopiles for absolute energy measurements, and is discussed in section 5.

If the beam to be measured is of uniform energy distribution, and if it is of suitable dimensions, a surface thermopile offers the simplest means for absolute energy measurement. Variations in sensitivity over the surface make certain precautions necessary, which are discussed under section 6.

If the beam of light may be focused to a spot not more than 5 mm. in diameter, a single thermocouple of the Beckmann and Dickinson type,⁶ with a single receiver large enough to include the entire beam, may be employed.

For beams of varying size and intensity distribution, a line thermopile of the many-junction type, operated by the methods described in this paper, provides a satisfactory means of absolute energy measurement.

In the case of line thermopiles, an integration process, as described in section 7, must be carried out in order to obtain absolute energy values. To simplify this process, it is important that the length of the sensitive portion of the pile be equal to or slightly greater than that of one dimension of the beam—preferably the dimension showing the most uniform distribution of intensity.

The integration process may be further simplified by using radiation receivers as wide as is compatible with uniform sensitivity over their surface.

We have experimented with several types of construction with this end in view. The construction shown in Fig. 1 enables one to use receivers up to 3 or 4 mm. wide without loss in uniform sensitivity. The junctions are of silver and bismuth wire, 0.05 mm. and 0.1 mm. diameter, respectively, the receivers of tin foil, about 0.02 mm. in thickness. The center receivers are each 3 to 4 mm. wide by 2 mm. high, the balancing receivers on the dark junctions are exactly half the area of the center receivers.

⁷ Moll and Burger: *Z. Physik*, **32**, 575 (1925); Moll: *Physica*, **6**, 233 (1926).

⁸ Brackett and McAlister: *Rev. Sci. Instruments*, **1**, 181 (1930).

⁹ Petit and Nicholson: *Astrophys.* **56**, 295 (1922); **68**, 279 (1928); Petit: *Carnegie Inst. Wash.*, Year Book, 140 (1929).

¹⁰ Beckmann and Dickinson: *J. Am. Chem. Soc.*, **52**, 126 (1930).

Welding and mounting are accomplished after the directions of Coblenz.¹¹ A silver, then a bismuth wire of the proper lengths are welded in two places to each center receiver (Fig. 1, b). Then two pieces of foil of half size are welded to the silver wire, about 1 cm. from each edge of the center receiver. Next these individual junctions are mounted, by means of the extending silver wires, on an ivory or bakelite block, as described by Coblenz. The final welding of adjacent junctions may be accomplished by carefully setting a glass plate mounted on a firm base, of just the size of the opening in the

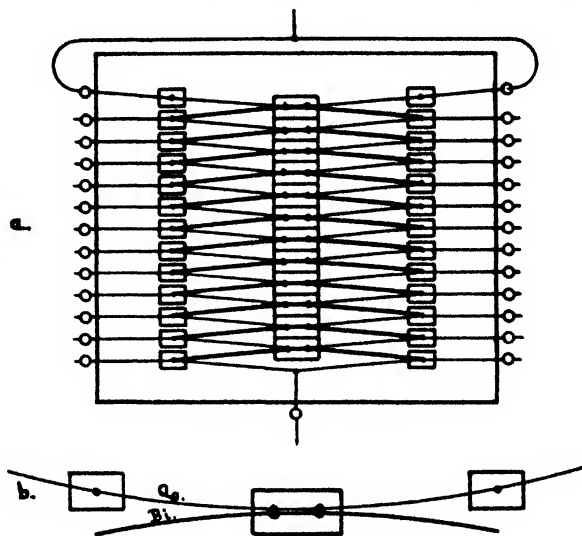


FIG. 1

Construction of Thermopile with Wide Radiation Receivers.

block, directly behind and in contact with the junctions. The bismuth wires from one junction are then welded to the silver wires of the next junction, care being taken that the weld is in the center of each small piece of foil previously attached to the silver.

Daniels¹² has designed and constructed thermopiles with receivers of silver foil, sufficiently heavy so that their width may be extended to 10 mm. while still retaining a uniform sensitivity over their surface. The heavier receiver extends the period of response of the thermopile, which allows time for a fairly uniform temperature to be attained throughout the receiver, no matter what part of it is exposed. It is necessary to use these piles in a thermostat.

In the case of line thermopiles, as will be shown in section 5, it is absolutely essential to choose an instrument which is or may be fitted with a slit narrower than and very close to the radiation receivers. For this reason some types of commercial line thermopiles are not to be recommended for absolute energy measurements.

¹¹ Coblenz: Bur. Standards Bull., 9, 15 (1913).

¹² F. Daniels: private communication.

2. Avoidance of Errors due to Drift

A thermopile-galvanometer combination which is sufficiently sensitive to measure beams of monochromatic light of average intensity is naturally very responsive to small changes in temperature, air currents, and similar disturbances. On a bismuth silver thermopile with 20 junctions and a galvanometer of sensitivity $15 \text{ mm}/\mu\text{v}$, a difference of 10^{-4} degree between hot and cold junctions should produce a deflection of approximately 1 cm. on a scale 5 meters distant from the galvanometer.

These disturbances result most commonly in a slow drift of the "zero point" of the galvanometer. The drift may be greatly reduced or avoided entirely by evacuating or thermostating the thermopile. There is, however, usually an additional drift produced on exposure to light, due to conduction along the wires to the cold junctions, Peltier effect, etc., so that even when a pile is completely protected, after exposure to light it requires some time to return to the original zero.

The errors due to both types of drift may largely be avoided by what has been termed the "ballistic" or "swinging equilibrium" method of reading.¹³ This differs from the method of reading with a ballistic galvanometer, in that a condition of swinging equilibrium is established by proper manipulation of a shutter between the light source and the thermopile. The shutter is first opened, then at the instant the mirror reaches a maximum deflection it is closed, the instant a minimum is reached it is again opened, and so on. With a thermopile of the Coblentz type these alternate maxima and minima will be reached within the period of the average d'Arsonval galvanometer—say three to five seconds. After allowing one or two complete swings in order to attain maximum amplitude, readings of maxima and minima are taken, then the average of two successive minima is subtracted from the intermediate maximum.

As shown by the accompanying actually recorded example, a considerable drift during the course of a set of readings has little effect on the actual deflection as obtained by this method.

Min.	Av.	Max.	Def.
34.8	35.0	54.3	19.3
35.2			
	35.5	54.6	19.1
35.8	36.0	55.2	19.2
36.2			
	36.35	55.5	19.15
36.5	36.6	55.8	19.2
36.7			

Av. = 19.19

¹³ P. A. Leighton and G. S. Forbes: *J. Am. Chem. Soc.*, **51**, 3551 (1929).

Ordinarily, about one minute is required to obtain a set of readings of five maxima and six minima, giving five values of the deflection, which may be averaged to give a very reproducible figure.

The foregoing method cannot be applied to thermopiles with periods longer than the period of the galvanometer. With such thermopiles it is necessary for the galvanometer to come to rest both for the maximum and minimum reading, and thermostating of the pile is essential to accuracy.

With a low resistance d'Arsonval galvanometer (such as Leeds and Northrup Type HS 2285x, C. D. R. 5Ω , I.R. 18Ω , period 7 sec. and sensitivity $15.3 \text{ mm./}\mu\text{v.}$), easily readable swing maxima and minima are obtained when the thermopile resistance or external resistance is greater than the critical damping resistance, ratios of as high as six fold having been found satisfactory. The precautions required by the variation in sensitivity at different positions of the galvanometer mirror (section 8) could be avoided by using the galvanometer as a null instrument, but the effect of drift in the thermopile E.M.F., we believe, can be eliminated more simply by observing deflections at swinging equilibrium. Moreover, if the light-flux being measured is itself subject to fluctuations during the course of a swing, the resulting deflection will tend to represent the integrated intensity during the short exposure.

3. Calibration

If the thermopile is calibrated by means of standard carbon lamps, as furnished by the Bureau of Standards, two sources of error (assuming that the absolute intensity of the radiation reaching the thermopile window from the standard lamp is accurately known) are to be considered. These sources of error arise from the conditions that:

1. The thermopile is usually calibrated in radiation of one wave length and used for another.
2. The thermopile may be calibrated for one range of galvanometer deflections and used for another.

The calibration in one wave length and use in another involves the question of non-selectivity of the absorbing surface. A carefully prepared platinum-black, lamp black,¹⁴ or bismuth black¹⁵ surface may safely be assumed as non-selective in absorption throughout the ordinary range of ultra-violet, visible, and near infra-red radiations. Such a surface will reflect a small amount, about 0.5 to 1.5% of the incident radiation,¹⁴ and variation in the amount of this reflection with wave length will produce some error, but the error will in general be of the second order and may be neglected. On the other hand, we have found some commercial thermopiles to give values as much as 20% too high when calibrated in the visible and infra-red of the carbon lamp and used for λ 2500Å or shorter in the ultra-violet. If the radiation receivers are not apparently perfectly black to the eye, they should be re-blackened. In most cases smoking with a sperm candle will suffice.¹⁴

¹⁴ Coblenz: Bur. Standards Bull., 9, 283 (1913); 11, 98 (1914); 12, 510, 522 (1916).

¹⁵ A. H. Pfund: Rev. Sci. Instruments, 1, 397 (1930).

Calibration in one wave length and use in another also involves a correction for changes in absorption and reflection of the thermopile window with wave length. On account of this change with wave length, the window will reflect and absorb different amounts of the standard lamp radiation for each current input.

The transmission of the thermopile window should therefore be measured not only for every wave length for which it is to be used, but also for every current input of the standard lamp radiation. In the case of the standard lamp radiation, these measurements of window transmission should not be made with a thermopile which is already protected with another window, but on an uncovered thermopile. Very careful shielding to avoid drift due to air currents will be necessary when the window is removed.

We have calculated the reflection and absorption losses to be expected for a crystal quartz window 1 mm. thick, when placed in the radiation from a standard carbon lamp burning at the four different current inputs at which it was calibrated. These calculations were made as follows:

1. The color temperature was estimated from measurements of the brightness temperature as made by an optical pyrometer. From this the spectral energy distribution of the radiation from the carbon filament was calculated from the radiation laws.

2. This spectral energy distribution was corrected for absorption by the glass bulb, using the data of Coblentz.¹⁶

3. The reflection of quartz, using Fresnel's law, and the absorption of 1 mm. of quartz, using Coblentz' data, were calculated for a series of points in the wave length region covered by the standard lamp.

4. The net loss was calculated from the losses at each wave length and the spectral energy distribution of the radiation.

A set of these calculations, for a carbon lamp burning at 1000°K, and the final results for four temperatures in the range usually covered by these lamps, are given in Tables I and II.

TABLE I

Standard Carbon Lamp at 1000° K

Radiation region μ	Total radiation below 4.0 μ	Trans- mitted by glass wall of lamp	Resulting radiation transmitted through glass	Amount reflected by quartz window	Amount absorbed by quartz window	Amount of total radiation reflected	Amount of total radiation absorbed
4.0-3.5	21%	4.3%	1.7%	7.5%	5%	0.13%	0.08%
3.5-3.0	23	27	12	7.8	2.0	0.93	.24
3.0-2.5	24	71	33	8.15	0.8	2.69	.27
2.5-2.0	17	85	26	8.4	0.5	2.18	.13
2.0-1.5	11	89	19	8.6	0.2	1.63	.04
1.5-1.0	4	90	7	8.8	—	0.61	—
1.0-0.5	0.6	90	1	9.0	—	0.09	—
	100%		100%			8.26%	0.76%

¹⁶ Coblentz: Bur. Standards Bull., 9, 116 (1913).

TABLE II

Reflection and Absorption Losses by 1 mm. Quartz Window in Radiation from Carbon Filament Lamp in Glass

Carbon Filament Temperature	Quartz Window 1 mm. thick		
	Reflects	Absorbs	Total Loss
1000° K	8.26%	0.76%	8.97%
1200	8.34	0.69	8.97
1400	8.44	0.56	8.96
1600	8.61	0.36	8.94

It is worthy of note that the changes in reflection and absorption with different current inputs are in opposite directions and almost exactly balance. Accordingly, for a good quartz window of 1 mm. thickness the transmission factor may be taken as a constant for carbon lamp radiation, regardless of current input. Most quartz windows will closely approximate the results given in Table II, but for the greatest accuracy the transmission should be directly determined for each window which is to be used. For example, as compared with our calculated value of 8.96%, Coblenz¹⁷ gives 8.5%; we have found a range of values from 8.3% to 9.1%; while Beckman and Dickinson¹⁸ give 9.4% for a window of unspecified thickness.

In the visible and ultra-violet region, down to 2000Å, only the reflection correction need be considered for crystal quartz. If the same window be used in calibration and in measurement, the correction to be applied is the ratio of

$$\frac{\text{Fraction of standard lamp radiation transmitted}}{\text{Fraction of radiation to be measured transmitted}}$$

The observed galvanometer deflection or energy calculated therefrom should be multiplied by this correction, the values of which for the principal lines of the mercury arc are given in Table III. A series of observed values for an average window are also included.

TABLE III

Quartz Window
Reflection Losses and Corrections for Mercury Arc Lines

Wave Length Å	Quartz Window		Thermopile Correction Factor (calculated values)
	Calculated	Reflects Observed	
Std. lamp radiation	8.96%	9.0	—
5770	9.2	9.2	1.003
4350	9.5	9.4	1.006
3663	9.7	9.5	1.008
3130	10.2	10.3	1.014
2654	10.5	11.5	1.017
2537	10.9	12.0	1.022

¹⁷ Coblenz: Bur. Standards Sci. Papers, 237 and 401.

¹⁸ Beckman and Dickinson: loc. cit.

At shorter wave lengths, the observed values usually become higher than the calculated values. This illustrates again the importance of measuring the transmission directly for each window at every wave length used.

The second source of error to be considered in calibration arises from the fact that the thermopile may be calibrated over one range of galvanometer deflections and used over another. Our experience has shown that in very few cases is it safe to assume a linear relationship between incident energy and deflection produced, over any great range of deflections. Each thermopile-galvanometer combination shows a different set of characteristics and must be calibrated over the entire range in which it is to be used. As an illustration, Table IV shows the number of ergs per centimeter of deflection for a series of energies for two typical thermopiles.

TABLE IV
Variations in Sensitivity with Size of Deflection

Cms. Deflection Scale Dist. 5 meters	Total Energy on Pile, Ergs		Ergs per Cm. Deflection	
	Pile No. 1 Surface 24.15 mm ²	Pile No. 2 Surface 314 mm ²	Pile No. 1	Pile No. 2
2	30	182	15.0	91.0
4	59	358	14.7	89.9
7	101	619	14.4	88.4
10	144	874	14.4	87.4
15	216	1290	14.4	86.0
25	363	2090	14.5	83.6
40	585	3280	14.6	82.0
60	888	4900	14.8	81.7
100	1498	8170	15.0	81.7
150	2265	12300	15.1	82.0
200	3045	16450	15.2	82.2

Pile No. 1, a line thermopile of the Coblenz type, shows a fairly uniform sensitivity for the range 7 to 25 centimeters, with a decrease in sensitivity at very small deflections, and a fairly uniform decrease at larger deflections. Pile No. 2, a commercial surface thermopile, shows a very definite increase in sensitivity with deflection up to about 60 cms., followed by a slight decrease in sensitivity for deflections above 100 cms. In each case the energies in the range covered by the standard lamps are in italics.

We have employed three methods for extending the calibration over any desired range.¹⁹ All avoid any assumptions regarding distance. The first method is made possible by the fact that several energy outputs are known for a given standard lamp, and is based on the conclusion that regardless of distance these known energies should bear constant ratios to each other.

The pile is first calibrated with the lamp at the standard distance. If calibration for larger energies is desired, the pile is moved toward the lamp

¹⁹ Forbes: loc. cit., p. 490.

until the deflection obtained with the lowest current input is approximately doubled. From the calibration in the first position and the observed deflection, the energy now falling on the pile with this lowest current input may be calculated. Each energy value of the lamp is now multiplied by the factor,

$$\frac{\text{Energy flux with lowest current at new distance}}{\text{Energy flux with lowest current at standard distance}}$$

This gives the energy flux from the standard lamp for the higher current inputs at the new distance, and by comparing with the deflections produced the calibration is extended. This process may be repeated as many times as necessary. If two points on the new setting overlap the old setting each time, the accuracy is much increased.

The second method consists of setting up two lamps (not standards) alongside each other, with a shield in between and a shutter in front of each. The current in the lamps is so adjusted that either one alone gives a deflection in the range covered by the standard lamps. The energy flux from each lamp is thus calculated. Next the deflection produced when both shutters are opened simultaneously is measured, in which case the energy flux on the pile is the sum of the two single values. This process may be repeated with larger current inputs until any desired range is covered.

A third method which we have tried for extrapolating the calibration curve beyond the range of the standard makes use of a monochromatic source of constant intensity, as follows:

(1) Select a glass filter which transmits between 20 and 80% of light of the wave length available. With the source at such a distance that the incident and transmitted intensities, I_0 and I , fall within the range covered by the standard lamp, determine $I/I_0 = K$.

(2) Move the source to a position at which the new transmitted intensity, I' , is approximately equal to I_0 of the first position. Observe deflections produced by I' and I'_0 . As the absolute value of I' may be read from the curve already established, I'_0 follows as

$$I'_0 = I' \cdot (1/K),$$

where the only assumption is that $I/I_0 = K$ is independent of intensity. The calibration curve, relating deflection to absolute intensity, is thus extended to I'_0 . Further repetitions at increasingly greater intensities will obviously serve to extrapolate the curve as far as is required.

At five times the maximum intensity available from a standard lamp this method agreed with the other methods to within 1%.

Direct variation of the distance from the pile to the source, with assumption of the inverse square law, for extending the calibration to larger or smaller intensities is limited by the fact that the carbon lamp is not a point source. Trümpler²⁰ has shown that for linear sources of half length X and pile distance d the inverse square law becomes modified to

$$I_2/I_1 = d_1 (\text{arc tan } X/d_2) / d_2 (\text{arc tan } X/d_1),$$

²⁰ Trümpler: Z. physik. Chem., 90, 385 (1915).

but even this formula cannot be applied with accuracy to carbon lamps. As Table IV shows, an extension of the calibration to very small deflections is also necessary when these are to be used.

The sensitivity of the galvanometer will in many cases vary with the position of the mid-point of the swing. We have found cases where the sensitivity changed by as much as 1% for a displacement of 10 cms. of the mid-point or zero point on a scale 5 meters distant.

It is, therefore, very important that some definite "zero point" or "low point of swing" be chosen on the galvanometer scale, and that all readings, both in calibration and use, be made with the galvanometer so set that the low point of the swing comes close to this predetermined value. Since, when

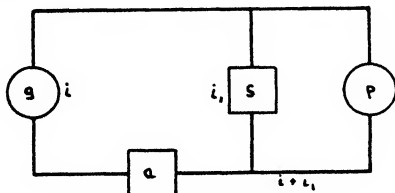


FIG. 2

Wiring Diagram for Shunt and Series Resistances.

using a constant "low point," the mid-point of the swing will vary with the size of the deflection, the sensitivity will also change with the size of the deflection, and this is undoubtedly a contributory cause to those changes of sensitivity discussed in the preceding paragraphs. This and other questions relative to calibration will be discussed in section 8.

4. Auxiliary Resistance Patterns

In case the light intensities to be measured are so high that deflections in excess of the total scale length are produced, it becomes necessary to incorporate in the thermopile-galvanometer circuit a suitable combination of shunt and series resistances.

The conventional scheme of connections is indicated in Fig. 2, where g is the galvanometer resistance, p the thermopile resistance, a the series, and s the shunt resistance. The same type of swing for all resistance patterns employed will be obtained by selecting such combinations of a and s that the resistance external to the galvanometer (i.e., "damping"), remains always the same as it was during the original calibrations. As the latter are usually carried out with the thermopile connected directly to the galvanometer, the desired condition requires an external resistance equal to the thermopile resistance, p . From the law of combination of resistances in parallel, it is obvious that the external resistance must be

$$a + \frac{1}{(1/s) + (1/p)} = \text{external resistance} = p. \quad (1)$$

Rearranging,

$$a = p^2/(p + s). \quad (2)$$

The question of extending the calibrations to include the auxiliary resistance patterns was first approached experimentally. As the result of numerous intercomparisons we have found that much labor can be saved by relating the sensitivity with an auxiliary pattern to the original calibration curve by means of the empirical equation

$$(E/E_o)_1 = a \text{ constant}, \quad (3)$$

where E_o = the intensity required to produce a certain deflection (or galvanometer current, i), with $a = 0$ and $s = \infty$, while E = the intensity required to produce the same deflection with some resistance pattern in which the relation in (2) is maintained. Our experimental results have proved equation (3) to hold independently of the magnitude of the deflection. This indicates that a linear proportionality exists between the thermopile E.M.F., π , and the incident light intensity, E . Thus, equation (3) may be expressed as

$$(\pi/\pi_o)_1 = (E/E_o)_1 = a \text{ constant}. \quad (4)$$

We now proceed to an evaluation of the ratio (π/π_o) in terms of the resistances, Fig. 2. Let i and i_1 be the partial currents through the galvanometer and shunt, respectively. The thermopile current is then $i + i_1$. When $a = 0$ and $s = \infty$, i_1 disappears and, from Ohm's law

$$\pi_o = i(p + g). \quad (5)$$

For any other resistance pattern with which the same galvanometer current, i , is produced by a thermopile E.M.F. = π , it follows from the laws of multiple circuits that

$$\pi = i(a + g) + (i + i_1)p. \quad (6)$$

Similarly,

$$\pi = i_1s + (i + i_1)p \quad (7)$$

Equating (6) and (7), and solving for i_1 ,

$$i_1 = i(a + g)/s. \quad (8)$$

Substituting for i_1 in (6),

$$\pi = i(a + g + p + (a + g)p/s). \quad (9)$$

Dividing by (5),

$$(\pi/\pi_o)_1 = \frac{as + gs + ps + ap + gp}{s(p + g)}. \quad (10)$$

Substituting the restricting equation $a = p^2/(p + s)$,

$$(\pi/\pi_o)_1 = p/s + 1. \quad (11)$$

Substituting for $(\pi/\pi_o)_1$ in terms of (4),

$$(E/E_o)_1 = p/s + 1. \quad (12)$$

In this final equation the galvanometer resistance has disappeared, and no function of the deflection appears, so that the constant $(E/E_o)_1$ may be cal

culated for any proper combination of resistances. As Table V shows, this theoretical expression accurately predicts the experimentally observed energy ratios for a variety of combinations. It thus becomes a very convenient relation to employ when the energies are such that resistance patterns must be used.

TABLE V
Energy Ratios for Various Resistance Patterns

P	s	E/E_0	
		Obs.	Calc.
10.3	7	2.4	2.5
10.3	4	3.7	3.6
36	21	2.76	2.72
36	7	6.3	6.2
31.6	7	5.5	5.5
31.6	11	3.8	3.9
31.6	21	2.5	2.5
28.8	11	3.62	3.62

The fact that this relation (12) holds over a wide range of deflections justifies the assumption made in its derivation that the pile gives a linear ratio of incident energy to E.M.F. produced, and indicates that the decrease in sensitivity always observed at high deflections (Table IV) is a function of the galvanometer and not of the thermopile. This is further indicated by the fact that even an intense beam of radiation falling constantly on the pile does not affect its response when simultaneously used to measure another, much weaker source of radiation, provided that the galvanometer suspension be so turned that the same zero point is obtained for all readings.

5. Effects of Diverging Light

In many cases it is desired to measure the absolute energy of a beam of light all portions of which do not strike the surface of the thermopile at perpendicular incidence. For example, in the laterally diverging beam of light behind a monochromator slit, the edges of the beam may deviate by several degrees from the direction of the central portion.

It is absolutely essential that all of the light which passes through the thermopile slit should fall on the radiation receivers. Light which misses the receivers is a dead loss. To avoid this, it is essential that the slit of the thermopile be placed close to (within 1 mm. of) the sensitive junctions, and that it be slightly narrower than the radiation receivers. With thermopiles in which this is not possible, a laborious correction must be made, and even with this correction no large degree of confidence can be placed in the results. This requirement necessitates some reconstruction in most commercial thermopiles.

The magnitude of the errors involved is shown by the three types of thermopiles indicated in Fig. 3. The upper figures show the relative positions of the radiation receivers, window, and slit in each case. The lower diagrams

show the relation between the sensitivity of the pile and the deviation from perpendicular incidence of the incident radiation. No. 1 was a vacuum thermopile, in which the slit was placed outside the vacuum jacket at a distance of 12 mm. from the junctions. This type of thermopile is useless for absolute energy measurements in diverging light. No. 2 was a line thermopile, with a slit of the same width as the receivers placed about 2 mm. in front of them, with the window in between. In this case it is possible to make corrections. No. 3, also a line thermopile, had receivers 3.3 mm. wide, and a slit 3.0 mm. wide (i.e., slightly narrower than the receivers) placed 0.8 mm.

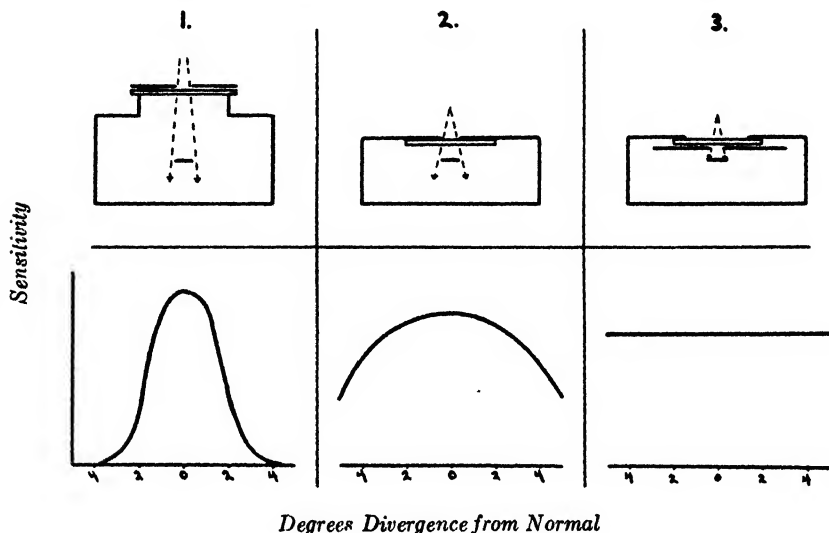


FIG. 3
Effects of Diverging Light on Three Types of Thermopiles.

in front, with the window on top. With this arrangement no change in sensitivity is produced by divergence up to 5° in either direction from the normal.

Although these illustrations all involve line thermopiles, the same considerations exactly apply to surface thermopiles.

6. Surface Variations in Sensitivity

If a spot of light of limited area be moved over the surface of a thermopile, the response produced will be found to vary with the position of the spot, and the smaller the area of this spot, the larger become the variations. Of the thirteen thermopiles which the authors have investigated, not one has proven an exception to this rule.

In the case of line thermopiles of the construction described in section 1 the chief variations to be considered are those along the long axis of the sensitive opening. These may be investigated by mounting an auxiliary slit of adjustable width in front of and at right angles to the thermopile slit, and placing the thermopile in a uniform beam of light, taking readings at interval

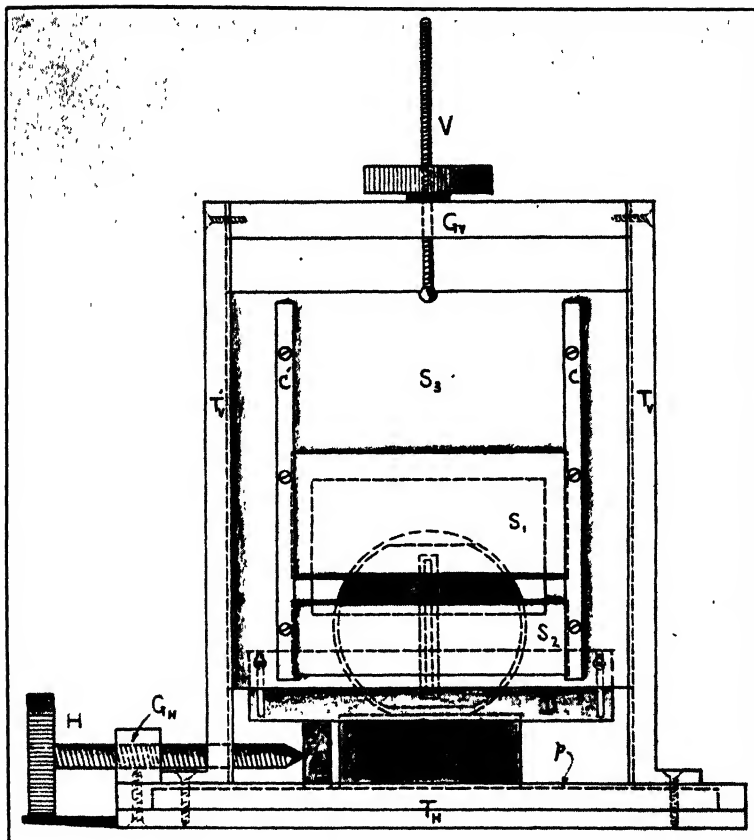


FIG. 4

Arrangement of Auxiliary Slit and Screw for Lateral Movement.

- S_1, S_2 = Jaws of Auxiliary Slit.
- T_v = Track for Vertical Movement of Auxiliary Slit.
- V = Screw for Vertical Movement of Auxiliary Slit.
- B = Base of Thermopile.
- T_h = Track for Lateral Movement of Thermopile.
- H = Screw for Lateral Movement of Thermopile.
- P = Thermopile Face.

as the auxiliary slit is moved along the thermopile slit. The details of such an apparatus are shown in Fig. 4, while in Fig. 5, the observed variations for two typical line thermopiles, obtained when an auxiliary slit 2 mm. wide was moved along the surface, are shown as a function of the linear distance along the thermopile slit.

The magnitude of the error produced by these variations is obviously a function of the uniformity of the beam of light to be measured. The radiation from the standard lamps may be considered as filling the entire sensitive opening of the thermopile, with a uniform distribution of intensity. If the measured radiation has the same characteristics, no error will be produced.

If, however, it is of variable intensity distribution, or if it fills only a portion of the sensitive opening, a correction must be made.

In the case of monochromator beams, the intensity distribution is most uniform in the direction parallel to the monochromator slit. By placing the slit of the line thermopile parallel to the monochromator slit, and by adjusting relative lengths so that the light beam as it reaches the thermopile slit is exactly the length of the slit, it follows that the error due to surface variations will be reduced to a minimum.

The authors have made and confirmed the interesting observation that, although the pile sensitivity may vary by $\pm 15\%$ along the length of the

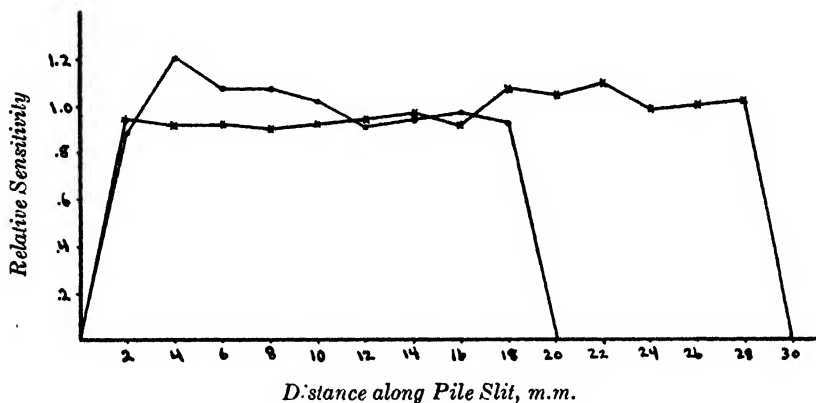


FIG. 5
Variations in Sensitivity along Surface for Two Thermopiles.

sensitive opening, in most cases even an irregular beam falling on the whole opening is fairly accurately integrated and its absolute energy given directly by the pile. A rather extreme case of this is illustrated in Table VI. Here E_n represents the energy as calculated from the observed response as a 2 mm. wide auxiliary slit was moved at 2 mm. intervals along the thermopile opening while exposed to a uniform beam of light. E_{av} is the average value of E_n , and r_n , the relative sensitivity at each setting, is the ratio of E_n to E_{av} . Similarly, E'_n represents the observed response at different settings of the auxiliary slit when the pile was placed in a non-uniform beam. These values may be corrected for the surface variations in sensitivity by dividing by the corresponding value of r_n in each case, as is done in the last column of Table VI. The close agreement between the sums of the uncorrected and the corrected values indicates that the thermopile in this case "smooths out" the irregularities in the beam and acts as its own integrator. We have found this to be generally true. If the slit be only partially illuminated, the error naturally becomes larger, but even if the beam be only half the length of the slit, in few cases does the error become greater than 1 to 2%.

This encouraging result for line thermopiles cannot be said to hold for surface thermopiles. The three commercial surface thermopiles investigated by the authors showed such tremendous variations in surface sensitivity that

TABLE VI

Energy Correction by Vertical Integration

Setting n	Uniform Beam		Relative Sensitivity r_n	Non-uniform Beam	
	E_n	E_{av}		E'_n	E'_n/r_n
1	78.6	89.2	0.88	141.9	161.0
2	107.9	"	1.21	142.3	118.0
3	95.3	"	1.07	95.3	89.3
4	95.3	"	1.07	55.9	52.5
5	91.1	"	1.02	40.1	39.3
6	81.7	"	0.91	45.8	50.5
7	83.9	"	0.94	62.1	66.1
8	87.0	"	0.97	56.9	58.4
9	82.8	"	0.93	48.2	52.0
				688.5	687.1

$$\text{Ratio, } \frac{E'_{\text{obs.}}}{E'_{\text{corr}}} = \frac{688.5}{687.1} = 1.002$$

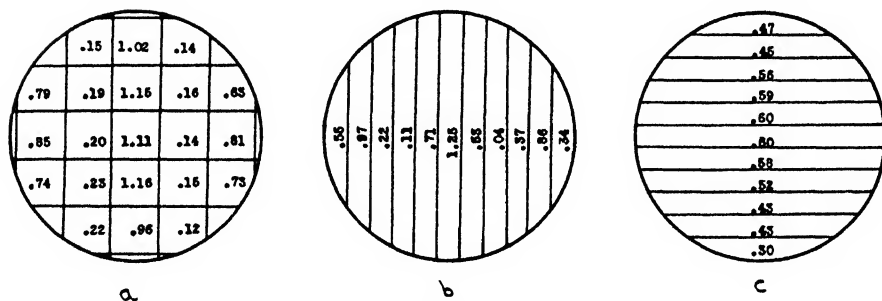


FIG. 6

Variations in Sensitivity over the Surface of a Surface Thermopile.

additional precautions become necessary. Fig. 6a is a typical example, and represents a surface thermopile with sensitive opening 22 mm in diameter, behind which 80 junctions were arranged in three rows. The pile was placed in a beam of uniform intensity, and a shield with an opening 4 mm. square moved across the face so that successive portions were exposed. The figures inserted in each portion represent the relative sensitivity, and were obtained by dividing the observed response by the area of that portion. Hence, the values given should be independent of the area exposed.

In Fig. 6b, a slit 2 mm. wide was moved at 2 mm. intervals across the face in a direction perpendicular to the rows of junctions, while in Fig. 6c the same slit was moved across the face in a direction parallel to the rows of junctions.*

As is clearly shown, the region about the center of each row of junctions is one of maximum sensitivity, while the region between each row is one of very low sensitivity.

* We are indebted to Mr. R. A. Mortensen for these measurements.

Here, as with line thermopiles, if the thermopile be calibrated with standard lamp radiation which is of uniform intensity over the entire sensitive surface, and if it be used for measurement of a uniform beam which just covers the whole surface, no error will be introduced by the surface variations. But if the cross section of the beam is smaller than the sensitive opening of the pile, or if it is of non-uniform intensity, the error will become appreciable. For example, in one case the uncorrected use of the pile for an elliptical beam 20 mm \times 10 mm in cross section resulted in an error of 22% in absolute energy values. Another example is given in Table VII, which shows the galvanometer deflection obtained when the thermopile was placed at different distances from the point of focus in a diverging beam, so that the area of the cross-section of the beam as it reached the pile was varied, while the total energy remained the same.

TABLE VII

Diameter of Exposed Area	Galvanometer Deflection	Diameter of Exposed Area	Galvanometer Deflection
22.0 mm.	77.9	14.3 mm.	84.8
20.7	80.3	13.0	95.1
19.4	77.7	11.7	104.7
18.1	76.6	10.4	114.9
16.8	76.7	9.7	130.2
15.6	79.4	7.8	145.7

The error produced when the beam is $1/2$ the diameter of the sensitive opening of the pile is about 45%.

Three methods of overcoming this error suggest themselves, viz.:

1. The radiation receivers may be covered with a disc of thin silver foil of the same size as the sensitive portion of the thermopile. The disc may be held in thermal contact with the junctions by means of a thin layer of shellac. The outer surface of the disc is blackened. Although this effectively reduces surface variations in sensitivity, it has the disadvantages of decreasing the total sensitivity of the pile and of prolonging the period, so that the swinging equilibrium method of reading cannot be used and it is necessary to thermostat the pile.

2. The thermopile may be converted to a line thermopile by shielding off all of the sensitive surface except a strip some 2 mm. wide along the center of the center row of junctions, and the energy of the beam integrated by the methods described in section 7. The thermopile so treated will not be as satisfactory as a simple line thermopile, because the unused junctions add unnecessarily to the resistance and materially increase the creep.

3. The cross section of a light beam from an ordinary prism monochromator usually shows a fairly uniform distribution of intensity in the direction parallel to the monochromator slit, and a shading off in intensity from center to edges in the lateral direction. Recalling that the thermopile is calibrated

in a beam of uniform intensity distribution which completely fills the sensitive opening, it is evident that errors due to surface variations will be minimized if:

a. The monochromator beam be adjusted to give maximum uniformity of intensity over its cross-section.

b. The thermopile be so turned that the direction of *maximum variation* in sensitivity of the pile shall coincide with the direction of *maximum uniformity* in intensity distribution of the light beam, in which case, of course, the direction of minimum variation in sensitivity will coincide with the direction of maximum variation in intensity distribution of the beam.

c. The thermopile be covered with a shield, set close to the junctions, of *exactly* the size and shape of the monochromator beam as it falls on the pile, and this shield be used both in calibration and measurement.

With these precautions, a surface thermopile will in many cases give reliable measurements of absolute energy. To illustrate, we have used a surface thermopile to measure the energy in a beam of λ 3130 Å emerging from a prism monochromator by method (2) in which the pile was used as a line thermopile, and by method (3) in which the pile was turned on its side and the slit used in (2) replaced by a shield with opening of the exact size and shape of the beam.

A. Results by method (2). (see section 7 for method of integration.)

Micrometer Screw Reading (across beam)	Galvanometer Deflection	Micrometer Screw Reading (across beam)	Galvanometer Deflection
0 mm.	0.70	10 mm.	45.14
2	17.50	12	42.93
4	30.86	14	33.38
6	36.87	16	13.20
8	42.37	18	0.47

Sum = 263.4

Deflection with standard lamp = 16.77 cm.

Radiation from standard lamp = 8.47 ergs/mm²sec.

Dimensions of slit = 1.9 × 22.15 mm.

Micrometer screw interval = 2.00 mm.

$$\text{Radiation from monochromator} = \frac{22.15 \times 2.00 \times 8.47 \times 263.4}{16.77} = 5900 \text{ ergs/sec.}$$

B. Results by method (3).

Deflection, trial 1. = 131.8 cm.

trial 2. = 131.9 cm.

Deflection, standard lamp = 71.7 cm.

Radiation from standard lamp = 8.47 ergs/mm²sec.

Area of thermopile opening = 380.7 mm².

$$\text{Radiation from monochromator} = \frac{380.7 \times 8.47 \times 131.8}{71.7} = 5930 \text{ ergs/sec.}$$

Summary:

Result, used as line thermopile = 5900.

Result, used as surface thermopile = 5930.

Difference = 0.5%.

Even with the precautions observed in method (3) measurements with a surface thermopile must be checked with a line thermopile, as was done in the example just given, before any degree of reliance may be placed on the results. The surface variations in sensitivity of a surface thermopile are too complex to make a correction practicable, and in general, an ordinary line thermopile will be found more satisfactory for absolute energy measurements.

7. Methods of Integration

For the measurement, with a line thermopile, of the total energy, in absolute terms, of a beam of cross section larger than the sensitive opening of the thermopile, it is necessary to take readings at intervals over the cross section of the beam and then to properly integrate these individual values to give the total energy.

The process is much simplified if the length of the sensitive opening be equal to or slightly greater than the diameter of the beam in the direction of maximum uniformity of intensity distribution (section 6). The thermopile is mounted on a sliding base so that the long axis of the slit is parallel to this direction of maximum uniformity, and so that it may be moved across the beam in a lateral direction.^{21,22}

If, now, the sliding base be equipped with a micrometer screw (Fig. 4) so that the readings may be taken at accurately known intervals, the procedure becomes still further simplified. If the intervals at which readings are taken are definitely known, it is only necessary to measure accurately the height or long dimension of the sensitive opening. Any desired width may be assumed for the sensitive opening, and the calculation is simplified by assuming the width is equal to the intervals through which the thermopile is moved. The following examples serve to illustrate this point.

Example A. Let us assume that a thermopile, with sensitive opening or slit exactly 1.5×20.0 mm. in size, is to be used to measure the total energy in a square beam 20×20 mm. in cross section, of uniform energy distribution. When exposed to any part of this beam so that the opening is fully covered, a deflection of 85 cms. is obtained. When exposed to standard lamp radiation of intensity $= 7.0$ ergs/mm²sec., a deflection of 10.0 cm. is produced.

1. Take the thermopile slit width as 1.5 mm. The standard lamp radiation falling on the pile is $1.5 \times 20 \times 7 = 210$ ergs/sec. As this produces a deflection of 10 cms., 1 cm. $\Delta = 21$ ergs/sec. falling on the pile (neglecting changes in sensitivity with size of deflection), which is equivalent to $21 \times 1/1.5 = 14$ ergs/sec. per mm. of beam width.

²¹ Villars: loc. cit., p. 330.

²² W. G. Leighton and G. S. Forbes: loc cit., p. 3141.

a. Moving the thermopile across the beam with the micrometer screw, take 20 readings 1 mm. apart. Each reading gives a deflection of 85 cm. Then, the total energy in the beam = $85 \times 14 \times 20 = 23800$ ergs/sec.

b. Take 10 readings, 2 mm. apart.

Total energy in beam = $85 \times 14 \times 2 \times 10 = 23800$ ergs/sec.

2. Assume the thermopile slit width is 1.0 mm. The standard lamp radiation falling on the pile then becomes by this assumption $1.0 \times 20 \times 7 = 140$ ergs/sec., or 1 cm. $\Delta = 14$ ergs/sec. falling on pile = 14 ergs/sec. per mm. of beam width.

a. Take 20 readings, 1 mm. apart.

Total energy in beam = $85 \times 14 \times 20 = 23800$ ergs/sec.

b. Take 10 readings, 2 mm. apart.

Total energy in beam = $85 \times 14 \times 2 \times 10 = 23800$ ergs/sec.

3. Assume the thermopile slit width is 2.0 mm. The standard lamp radiation falling on the pile, by this assumption, becomes $2.0 \times 20 \times 7 = 280$ ergs/sec., or 1 cm. $\Delta = 28$ ergs/sec. falling on the pile, which is equivalent to 14 ergs/sec. per mm. of beam width.

a. Take 10 readings, 2 mm. apart.

Total energy in beam = $85 \times 14 \times 2 \times 10 = 23800$ ergs/sec. And so on.

In each case the same value is found for the No. of ergs/sec. per mm. of beam width required to produce 1 cm. deflection, regardless of what assumptions are made regarding the width of the thermopile slit, and the same value for the total energy is obtained, regardless of these assumptions.

Example B. In this example is presented the actual measurement of a beam of monochromatic radiation, of non-uniform intensity distribution laterally, as determined by two different thermopiles.

Pile No. 1, Slit 30.50 mm. long, assumed 3.0 mm. wide.

Readings taken at exactly 1 mm. intervals. $\frac{\text{Reading interval}}{\text{Slit width}} = \frac{1}{3}$.

Standard lamp calibration gave the following factors:

Deflection, cms.	Ergs/sec. falling on pile per cm. Δ	Deflection, cms.	Ergs/sec. falling on pile per cm. Δ
3	47.4	75	47.3
10	47.2	100	47.4
25	47.2	125	47.4
50	47.3	150	47.5

The readings across the monochromatic beam were:

Setting	Galvanometer Deflection	Ergs/sec. on pile	Setting	Galvanometer Deflection	Ergs/sec. on pile
1	3.5 cms.	166	8	99.5	4715
2	13.6	642	9	85.6	4049
3	33.1	1563	10	66.2	3132
4	60.6	2868	11	40.2	1900
5	84.7	4006	12	19.3	911
6	101.2	4795	13	6.0	284
7	106.3	5040	14	1.5	71
					<hr/>
Sum =					34142

Total energy in beam = $34142 \times 1/3 = 11381$ ergs/sec.

Pile No. 2, Slit 24.38 mm. long. Assumed 1.0 mm. wide, and readings taken at exactly 1 mm. intervals. $\frac{\text{Reading interval}}{\text{Slit width}} = 1.$

Standard lamp calibration factors:

Deflection, Cms.	Ergs/sec. falling on pile per Cm. Δ	Deflection, Cms.	Ergs/sec. falling on pile per Cm. Δ
3	20.9	75	21.2
10	20.5	100	21.4
25	20.6	125	21.5
50	20.9	150	21.6

Readings across monochromatic beam:

Setting	Galvanometer Deflection	Ergs./sec. on pile	Setting	Galvanometer Deflection	Ergs./sec. on pile
1	1.5 cm.	31	8	74.0	1568
2	13.0	267	9	57.2	1198
3	33.6	696	10	40.7	847
4	56.1	1174	11	18.7	384
5	73.7	1562	12	3.3	69
6	81.3	1728	13	0.7	15
7	81.7	1737			
					Sum = 11276

Total energy in beam = $11276 \times 1 = 11276$ ergs/sec.

$$\frac{\text{Ratio, Pile No. 1}}{\text{Pile No. 2}} = \frac{11381}{11276} = 1.009.$$

Thus the integrated values obtained by the two piles, for the total energy in the monochromatic beam, differ by only 0.9%.

In a beam of this sort, readings may be taken at intervals greater than 1 mm. without materially disturbing the accuracy. This may be demonstrated from the example just given. For either thermopile, if readings had been taken at 2 mm. intervals, the alternative values of those given above would have been obtained, and if readings had been taken at 3 mm. intervals, every third value would have been obtained.

Thus, for thermopile No. 1,

Readings at 2 mm. intervals (alternate values from above set)

Total Energy in beam	Deviation from mean
Odd settings $17008 \times \frac{2}{3} = 11339$	0.3%
Even settings $17134 \times \frac{2}{3} = 11423$	0.3%

Readings at 3 mm. intervals (every 3rd value from above set)

Total Energy in beam	Deviation from mean
Settings 1, 4, 7, 10, 13 11490	0.9%
Settings 2, 5, 8, 11, 14 11334	0.4%
Settings 3, 6, 9, 12 11318	0.5%

For thermopile No. 2, readings at 2 mm. intervals,

Total Energy in beam	Deviation from mean
Odd settings $5623 \times 2 = 11246$	0.3%
Even settings $5653 \times 2 = 11306$	0.3%

The method just described may be termed the direct summation method of energy integration. For the greatest accuracy in the determination of total energy with a line thermopile, readings should be taken at short intervals, a curve of energy vs. setting drawn, and the area under this curve determined by graphical integration.

Fig. 7 represents a typical curve of this kind, for a beam of radiation issuing from a monochromator slit. The crosses represent thermopile readings. The direct summation method which we have illustrated in the preceding examples in effect takes the total energy of the beam as equal to the sum of the areas of the rectangles shown in Fig. 7, while the graphical method takes the energy as equal to the area under the curve. In the case illustrated, the area under the curve, or energy by graphical integration, was 9133 erg/sec., while the area of the rectangles, or energy by direct summation was 9130 erg/sec., a difference of 0.03%. If alternate readings (2 mm. intervals) are taken, the direct summation method gives 9175 erg/sec. for the energy, a difference of 0.46% from the graphical integration value.

The size of the interval between settings which may be used without material decrease in accuracy is a function of the width of the thermopile slit, the width of the beam, and the amount of variation in intensity across the beam. For narrow beams (less than 3 to 4 times the slit width) the interval should be equal to or less than the actual width of the thermopile

slit. For relatively wide beams, of the order of ten times the slit width, if no sharp changes in intensity distribution occur, intervals of several times the slit width may be used.

These methods assume that the thermopile is capable of acting as its own integrator in the long direction of the slit; that is, that a beam of radiation of variable intensity distribution along the slit, or covering only part of the slit, gives the same deflection as it would if the same amount of radiation were evenly distributed over the entire sensitive opening. The limitations

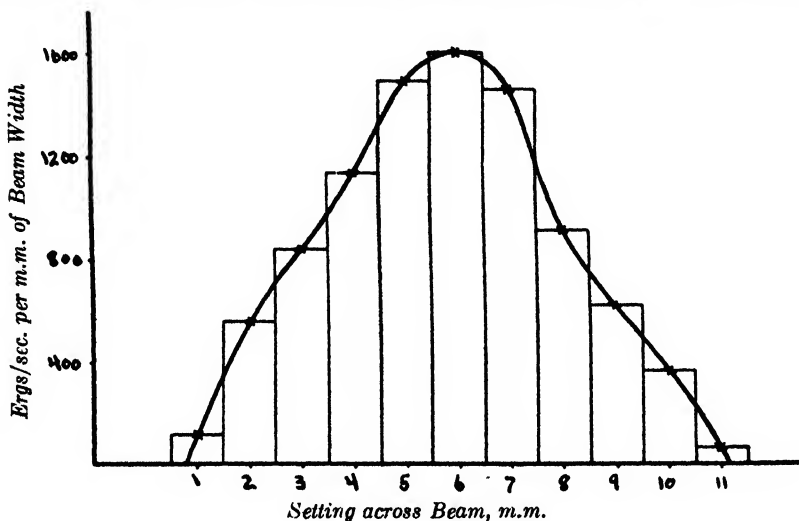


FIG. 7

Comparison of Graphical and Summation Methods of Energy Integration.

to this condition have been discussed in section 6. Precautions which must be observed in the direct integration of energy with a surface thermopile have also been discussed in section 6.

8. Variations in Sensitivity

Variations in sensitivity of the thermopile-galvanometer system with size of deflection, and with the position of the zero point on the scale, were discussed in section 3. The position of the zero point means, of course, the position of the mirror and moving coil with respect to the magnetic field. We have found the greatest sensitivity is produced when the mid-point of the swing finds the mirror parallel to the front face of the galvanometer, i.e., the coil parallel to the magnetic field. Changes from this point may produce as much as a 1% change in sensitivity for a 10 cm. shift in the zero point or mid-point of the swing on a scale 5 meters distant. On the other hand, quite considerable movements of the suspension adjustment, which may be necessary to obtain the same zero point for all readings, seem to be without marked effect on the sensitivity. To demonstrate, two carbon lamps were set up in front of a thermopile. Lamp A, fitted with a shutter, gave a deflection of approximately 29 cm., while lamp B, which radiated

continually on the pile while burning, produced a deflection of 120 cm. Deflections caused by "A" were observed with and without "B" burning, the mirror being always set to give the same low point of swing.

Deflection, without B (before) = 29.35 cm.

Deflection, with B burning = 29.35

Deflection, without B (after) = 29.30

That is to say, with four times its own energy effect constantly flowing through the pile and galvanometer, the source A produced a swinging deflection identical with that produced when no energy came from B. Accordingly, it is not necessary to worry about outside radiation of constant intensity which falls on the pile during calibration or use.

Thermopile-galvanometer systems in general show a slightly different response from day to day to the energy from a standard lamp. Temperature and humidity seem to be chief among the factors causing these variations. Why humidity should play a part is not known. It should not be due to the absorption of infra-red radiation by the water vapor. The variations are no doubt due, to some extent, to changes in the standard lamp radiation, and in part to changes in the sensitivity of the recording system. Thus it is not possible wholly to correct for them, and the magnitude of these changes marks the limit of accuracy which may be expected from this method of absolute energy measurement. A partial correction may be made by calibrating a well seasoned carbon lamp, burning at definite amperage, by direct comparison with the standard lamps, and using this lamp as a secondary standard to check the thermopile sensitivity every day that measurements are made. Two secondary standards mounted side by side behind a shield, with another shield between and a shutter in front of each, gives a still more accurate check, as the danger of error due to individual variations in lamp intensity is lessened.

Coblentz³ has suggested observation of the deflection produced by a known current generated by induction in the thermopile-galvanometer system as a means of checking the sensitivity. He also suggests the use of an induced current of known strength to attain the desired zero point and avoid drift. Usually the drift is too irregular to be avoided by any method of control except thermostating, but this suggestion is worthy of consideration in obtaining the desired zero point, if trouble should be experienced in obtaining it by moving the suspension.

In addition to day to day variations in sensitivity, slow changes extending over a considerable period are often experienced. Fig. 8 shows the variations in sensitivity of one thermopile-galvanometer system over a period of three years. Day to day variations were not included, the points given here representing average values. Experiments made over a period of several years also indicate that standard carbon lamps deteriorate somewhat both with use and age, and should be supplemented at intervals with new standards, at periods of not greater than three years.

³ Coblentz: Bur. Standards Bull., 9, 33 (1913).

In the "Instructions for using the Radiation Standards," issued with each radiation standard, the precaution is stated that "these lamps should be used as reference standards, and other lamps used as working standards. . ." This precaution cannot be over emphasized. It has been our experience, as illustrated in the following table, that a rate of deterioration of as much as $1\frac{1}{2}\%$ per hour of burning may be expected, at least during the first times the lamp is operated.

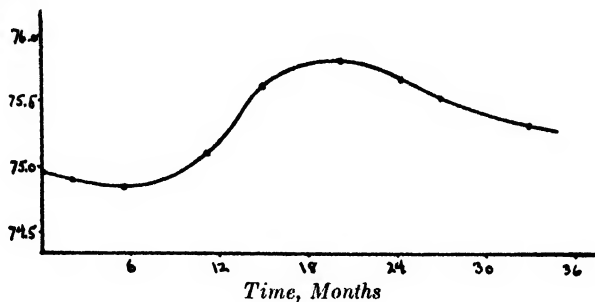


FIG. 8

Change in Sensitivity with Time.

TABLE VIII

Rates of Deterioration of Radiation Standards

Standard	Time of Burning	Deterioration	Rate per hour
C-39	9 hours	3.1%	0.35%
C-40	5 "	1.7%	0.35%
C-69	3/4 "	0.56%	0.75%
			Av. 0.5%

The above values were obtained as a result of a thorough inter-comparison of these three standard lamps, the calibration of C-69 being accepted as correct during the first few minutes of burning. The standards should best be used in pairs, so that any sudden deterioration of one lamp may be detected.

Summary

The measurement of the absolute intensity of visible and ultra violet light by means of a thermopile-galvanometer system has been discussed with particular reference to the conditions existing at the exit slit of a monochromator.

Various sources of error have been investigated, including those which are inherent in the galvanometer and in the thermopile, as well as certain sources of error created by employing a thermopile for the measurement of diverging light differing in wave length from that of the light from standard carbon filament lamps. Several important precautions have been emphasized, while, on the other hand, certain sources of error have been shown negligible. The advantages of linear thermopiles over certain surface piles of commercial make have been demonstrated.

The observation of galvanometer deflections under the conditions of "swinging equilibrium," successfully used by the authors and others at Harvard University and elsewhere, has been described. Details are included for integrating the total intensity of a light beam which presents a cross section greater than the active receiving area of the thermopile.

Three methods of extrapolating the thermopile-galvanometer sensitivity curve are outlined, none of these requiring the assumption of the inverse square law. A simple equation has been derived and verified experimentally which extends the calibration curve to include various resistance patterns useful at high intensities.

In concluding the authors wish to express their appreciation to Professor George Shannon Forbes of Harvard University under the direction of whom certain of the investigations in this paper were begun.

Thanks are also due Dr. Francis E. Blacet and Mr. Raymond A. Mortensen of Stanford University for some of the experimental data quoted, and to Dr. Curtis Haupt of Pomona College for his helpful criticism.

NOTE ON THE ABSORPTION OF OXYGEN BY SHEETS OF RUBBER

BY GEORGE A. LINHART

Very interesting and commercially very important experiments have recently been made in the Bell Telephone Laboratories by G. T. Kohman¹ on the absorption of oxygen by sheets of rubber. No attempt, however, was made to interpret the results mathematically. It is true, of course, that any empirical equation to express the course of the process would be merely a sort of garnish. It would be interesting, however, to show that these processes are not unique.

Some years ago the writer² published an equation which described the progress of many processes in the fields of chemistry, botany, biology, bacteriology, etc. The form of this equation is,

$$C = \frac{C_{\infty} b t^a}{1 + b t^a}$$

It is based upon the results of the tossing of a coin and represents in fact the law of uni-directional probability. The derivation of the equation is rather lengthy. In this note the equation will be applied to the process of the absorption of oxygen by sheets of rubber.

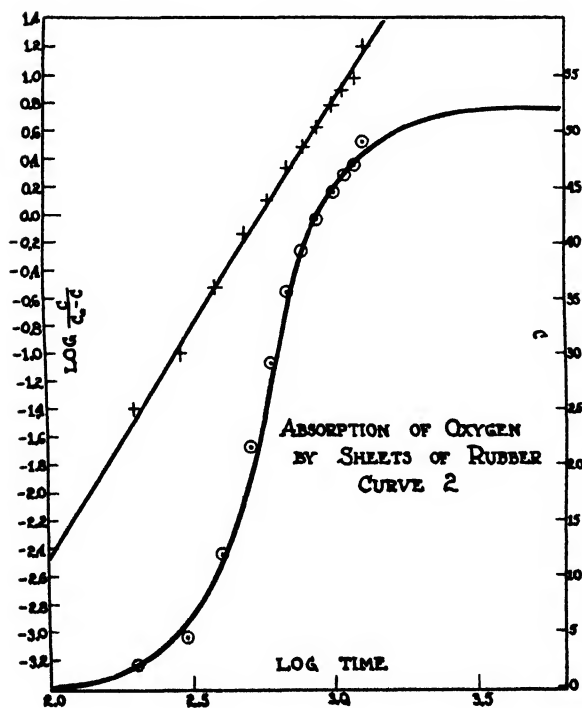
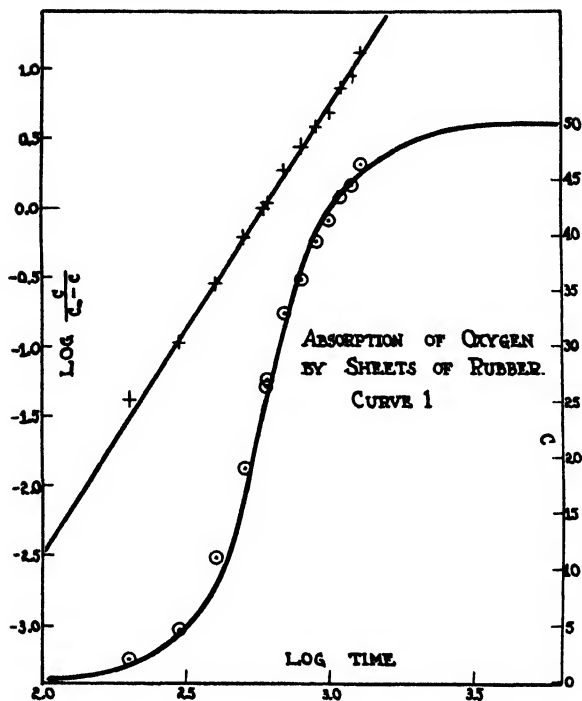
In the original article cited above the numerical data are not given, but they are so well shown on the graphs that the results may be read off to within one per cent. The amounts of oxygen, therefore, given in the table of this note are expressed in millimeters read off on the original graph, while the time is expressed in hours.

In Table I, C denotes the amount of oxygen absorbed at any time, t , and a and b are constants. Usually, a is the same for a given series of experiments even when the temperature varies, provided the other conditions are the same. However, in this note, the temperatures are the same, but the conditions under which each experiment is conducted are different, inasmuch as the sheets of rubber are subjected to different amounts of anti-agers. We should not, therefore, expect a to be the same for all experiments. Still, it does not differ to any great extent, as a glance at the table will show.

The equation in this note is of such nature that from the second differential with respect to $(\log t)$, we obtain the value for C_{∞} , since at this point (point of inflection with respect to $\log t$), $C = C_{\infty}/2$. In many processes

¹ J. Phys. Chem., 33, 226 (1929).

² Riverside Junior College Journal (Occasional Papers) May and June (1929); Eureka Junior College Journal (Occasional Papers) September (1921).



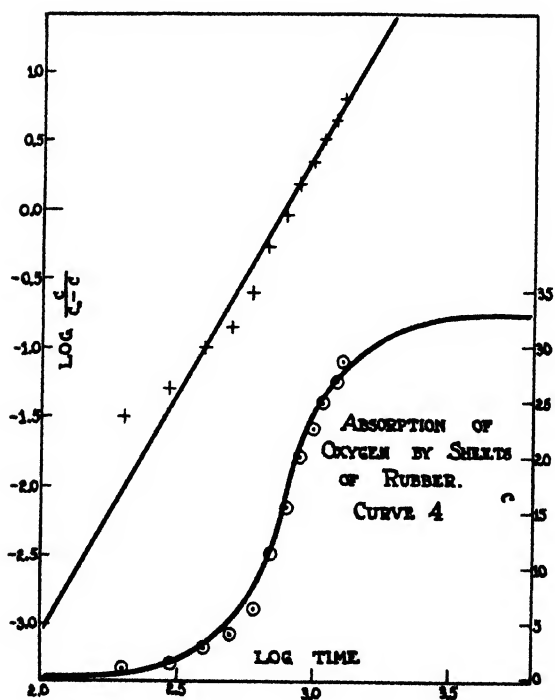
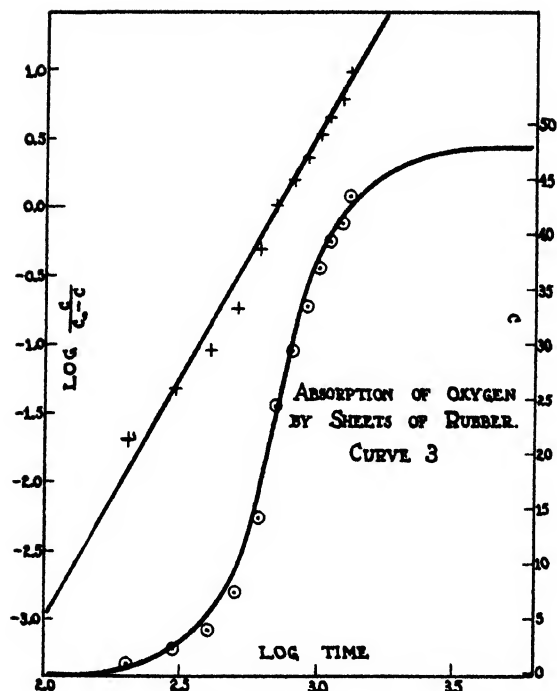


TABLE I

Figure 8 (original article)

t	Curve 1		Curve 2		Curve 3		Curve 4	
	a = 3.296		a = 3.257		a = 3.490		a = 3.465	
	log b = -9.15901		log b = -8.99790		log b = -9.94334		log b = -10.01614	
	C(obs.)	C(calc.)	C(obs.)	C(calc.)	C(obs.)	C(calc.)	C(obs.)	C(calc.)
200	2.0	1.30	2.0	1.6	1.0	0.6	1.0	0.3
300	4.6	4.55	4.6	5.5	2.3	2.3	1.6	1.2
400	11.0	10.36	12.0	12.0	4.0	5.8	3.0	3.0
500	19.0	17.65	21.5	19.9	7.5	11.1	4.0	6.1
600	26.5	24.50	29.0	27.5	16.0	16.8	6.5	9.6
700	33.0	31.15	35.5	33.8	24.5	22.6	11.5	13.5
800	36.5	35.90	39.0	38.6	29.5	29.1	15.5	18.9
900	39.5	39.55	42.0	42.0	33.5	33.6	20.0	20.6
1000	41.5	42.15	44.5	44.5	37.0	37.0	22.5	23.3
1100	44.0	44.00	46.0	46.3	39.0	39.6	25.0	25.4
1200	45.0	45.35	47.0	47.6	41.0	41.5	27.0	27.0
1300	46.5	46.35	49.0	48.5	43.5	42.9	28.5	28.3
..		50.00		52.0		48.0		33.0

C_{∞} is known at the start. For example, in a chemical reaction, C_{∞} is the initial concentration of the reacting substance. In other cases, C_{∞} is only approximately known and is therefore given more accurately by the point of inflection. This is obvious from the symmetry of the curve where C is plotted against $\log t$. The straight line plots are obtained by transforming the equation given above into the logarithmic form,

$$\text{Log} \frac{C}{C_{\infty} - C} = a \text{Log } t + \text{Log } b$$

Considering the difficulty of controlling conditions in heterogeneous systems such as these, the agreement between the observed and calculated values is quite satisfactory.

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CATALYTIC OXIDATION OF n-PROPYL ALCOHOL

ALLAN R. DAY AND ABNER EISNER

It is a well-known fact that ceric oxide acts as a powerful oxidizing catalyst, especially where the process is one of vapor phase oxidation. Ceric oxide is often recommended for this purpose in the combustion method for the determination of carbon and hydrogen. A better example is the great increase in light emissivity of thoria mantles when mixed with 0.9 per cent of ceric oxide. Swan¹ has shown that the greatest efficiency in the catalytic oxidation of electrolytic gas occurs at the same concentration of CeO_2 in ThO_2 (i.e. 0.9 per cent). It is probable that the CeO_2 by acting as an oxygen carrying promoter brings about more rapid combustion and consequently higher temperatures.

In a previous paper² it was shown that this property was shared by the other rare oxides including the more basic La_2O_3 . The great activity of these oxides makes it practically impossible to use them for the partial oxidation of organic compounds. Their use in small amounts with other less active oxidation catalysts should prove to be practical. A recent patent³ has made use of such a combination. The patent recommends the use of a catalyst comprised of copper mixed with not more than 1 per cent of ceric oxide for the preparation of acetaldehyde from ethyl alcohol.

In a recent paper⁴ the use of metallic silver alone and mixed with small amounts of samarium oxide as catalysts for the oxidation of ethyl alcohol was outlined. The results, while indicating that small amounts of the rare earth oxide did exert a promoter effect on the production of acetaldehyde, were scarcely definite enough to draw any general conclusions.

The results presented here on the oxidation of n-propyl alcohol confirm the conclusions of the above mentioned paper. It is shown that Sm_2O_3 when present in small amounts with silver does act as a promoter in the partial oxidation of n-propyl alcohol to propionaldehyde.

Experimental

The apparatus used was essentially the same as that used in the previous work. A wet-test meter was attached at the end of the absorbing train to measure the total volume of outlet gases. A gas-sampling tube was also placed in line and the mixed gases were analyzed in a modified Orsat. The temperature of the preheater was so regulated that the mixture of air and alcohol left the coil at a temperature of 125°C . Preliminary runs showed that the highest

¹ J. Chem. Soc., 125, 780 (1924).

² Lowdermilk and Day: J. Am. Chem. Soc., 52, 3535 (1930).

³ Brit. 344,554, Dec. 16, 1929.

⁴ Day: J. Phys. Chem., 35, 3272 (1931).

aldehyde conversions were obtained at a thermostat temperature of $71^{\circ}\text{C}.$, indicating this to be the optimum vaporization temperature for the formation of propionaldehyde.

The oxidation process was carried out by passing measured quantities of dry, carbon dioxide free air through the vaporizer containing the *n*-propyl alcohol which was maintained at constant temperature by means of a thermostat. The alcohol-air mixture was then passed through the preheater and into the catalytic chamber, the catalyst having been previously heated to $350^{\circ}\text{C}.$ The heat of reaction was sufficient to maintain the reaction after it had once started. The catalyst temperatures were measured by means of a thermocouple. The latter was protected by means of a quartz jacket which was imbedded in the catalyst. The catalyst chamber (length 15 mm., diameter 17 mm.) was filled with the impregnated 12 mesh pumice. The length of each run was carefully timed by means of a stop watch. The products of the reaction were collected in absorption flasks which were part of the cooling system. The flasks were then emptied, rinsed and the resulting solution diluted to a definite volume. Aliquots of this solution were taken for analysis.

The following types of catalysts were employed:

- A. 2.7928 g. of silver (equivalent to 3 g. of Ag_2O) deposited on 9 cc. of 12 mesh pumice.
- B. 2.7894 g. of silver (equivalent to 2.99625 g. of Ag_2O) and 0.00375 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.
- C. 2.7858 g. of silver (equivalent to 2.9925 g. of Ag_2O) and 0.0075 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.
- D. 2.7788 g. of silver (equivalent to 2.985 of Ag_2O) and 0.015 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.
- E. 2.7648 g. of silver (equivalent to 2.97 g. of Ag_2O) and 0.03 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

It will be noted that catalysts B, C, D and E contain 0.125, 0.25, 0.5 and 1 per cent of samarium oxide respectively based upon $\text{Ag}_2\text{O}:\text{Sm}_2\text{O}_3$. The catalysts were prepared in the same manner as the catalysts used in the earlier work. Before use they were activated by heating in a stream of *n*-propyl alcohol vapor and air for an hour. Their efficiency as catalysts did not increase over longer periods of activation. Duplicate catalyst preparations were used for many of the runs and excellent check results were obtained, indicating the uniformity of the catalysts used.

Pure *n*-propyl alcohol (sp.g. $0.804^{20^{\circ}}$) was used for all experiments. Approximately 15 g. of alcohol was passed over the catalyst during each run.

Determination of Propionaldehyde.—The aldehyde was determined by Ripper's bisulfite method.

Determination of Propionic Acid.—To a definite amount of standard sodium hydroxide solution was added a little barium chloride solution and a few drops of phenolphthalein. The resulting solution was then titrated with a portion of the condensate until the red color was discharged.

Gas Analysis.—The gas sample was transferred from the sampling tube to the Orsat and the usual methods employed for the determination of carbon dioxide, oxygen, alkenes and carbon monoxide.

The following table includes the results for the more important runs. Duplicate runs checked within 0.5 – 0.6 per cent (based on the aldehyde yields) and they are therefore not included in the table.

TABLE I
Thermostat Temp. 71°C

	Air Rate Liter/min.	Catalyst Temp. °C	Molar Conversions		
			Aldehyde %	Acid %	CO ₂ %
A	0.94	505	71.5	3.5	4.2
	0.77	450	72.3	3.5	4.0
	0.65	395	72.1	3.3	3.4
	0.52	355	72.8	3.4	4.1
B	0.77	445	73.9	3.5	4.0
	0.65	390	75.4	3.4	2.7
	0.52	365	76.4	3.2	4.0
C	0.94	495	71.5	3.8	3.2
	0.77	455	72.6	3.6	4.1
	0.65	420	74.3	3.5	4.1
	0.52	380	75.5	3.4	4.2
D	0.94	498	70.0	4.1	2.0
	0.77	445	71.3	3.6	3.2
	0.65	385	74.0	3.6	2.7
	0.52	350	74.3	4.2	3.5
E	0.94	491	69.0	3.4	5.0
	0.77	460	71.4	3.3	3.8
	0.65	395	72.4	3.4	3.8
	0.52	345	73.1	3.6	4.5

Discussion of Results

There does not appear to be a careful study on the oxidation of n-propyl alcohol in the literature since the work of Orlov.¹ Orlov using metallic copper as the catalyst reported 50 per cent as his highest yield of propionaldehyde.

The results recorded in Table I show that the maximum conversions to aldehyde were obtained where the lower air rates were used. The results recorded for catalysts B and C show definite increases in the conversion to aldehyde. Even with catalyst D an increase in yield is shown where the lower

¹ J. Russ. Phys.-Chem. Soc., 40, 203 (1908).

air rates were used (0.65 – 0.52 L/min.). It will be noted that while the yields of aldehyde were definitely higher, the amount of carbon dioxide formed did not appear to increase. This would indicate that small amounts of Sm_2O_3 do not promote complete oxidation under the conditions recorded in Table I, in spite of the fact that an excess of oxygen was present during the runs. At the thermostat temperature of 71°C . the ratio mols alcohol/mols O_2 was approximately $1/0.57$ – 0.58 (theoretical $1/0.5$).

At higher catalyst temperatures (higher air rate used) the samarium oxide did exert a promoter effect toward complete combustion. The amount of carbon dioxide increased with increase in temperature much more rapidly than in the cases where pure silver was used. However, one would not work at such temperatures if propionaldehyde were the desired product. The results in the table show that within certain catalyst temperatures (350 – 500°) the small amounts of Sm_2O_3 present did not enhance or produce any undesirable side reactions. The amounts of carbon monoxide and alkenes formed were not included in the table as they were in every case negligible quantities.

Summary

1. The optimum conditions for the oxidation of n-propyl alcohol to propionaldehyde, using metallic silver on 12-mesh pumice, have been determined.
2. It has been shown that the presence of small amounts of samarium oxide increases the yields of propionaldehyde.
3. Higher yields of propionaldehyde have been obtained by a one-step vapor phase oxidation of n-propyl alcohol than have been previously reported from similar methods.

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THE VARIATION OF THE SURFACE TENSION OF AQUEOUS SOLUTIONS OF CERTAIN COMPLEX ORGANIC SUBSTANCES WITH TIME

BY J. C. GHOSH AND MADHAB CHANDRA NATH

The growth of films on the surface of aqueous solutions of a number of organic dyes was first recorded by Rhode.¹ His method consisted in the suspension of a sheet of metal in the dye solution by a fine wire. Torsion was applied until the surface was broken. The angle of torsion was a measure of the thickness of the film, and the rate at which the torsion necessary for tearing up the film increases with time is a measure of the rate of growth of film. He concluded that the dyestuffs which in solution, show photo-electric effect, have the characteristic property of forming a film on the surface, the maximum photo-electric effect being obtained when the film-thickness becomes a maximum.

It is also possible that aqueous solutions of organic complex substances may show the gradual formation of surface-film and it appears that if a method could be devised for recording the variation of surface tension of aqueous solutions of these substances with time, some insight can be gained into the kinetics of the molecular processes which are responsible for producing a film on the surface. It is to be expected that with the growth of film on the surface, the surface tension of the solution should gradually diminish, arriving at a constant value when the growth of the film is at an end.

Indications are not wanting that the nature of the surface of a solution immediately after it is created is different from that of the surface after a certain time has elapsed and conditions of equilibrium have been established. This is specially true in the case of hydrophylic sols like sodium oleate, gelatine, egg-albumin, saponin, etc. For these sols investigations of Rayleigh² and Berczeller³ have shown that the surface tension measured by a dynamic method (where the surface tension of a freshly created surface is measured) is always considerably greater than that measured by a static method. The variation of surface tension of certain colloidal solutions with time has been measured by du Noüy,⁴ and Johlin.⁵

According to Freundlich, "the method of adhesion rings is to be particularly recommended for determining the surface tension of any plane liquid surface, which it is desired to disturb as little as possible." In the experi-

Ann. Physik, (4) 19, 935 (1906).

Proc. Roy. Soc., 47, 281 (1890).

Intern. Z. physik. chem. Biol., 1, 124 (1914).

Phil. Mag., [6] 48, 264 (1924).

J. Phys. Chem., 29, 1129 (1925).

ments to be described in the following pages, the ring-method has been suitably modified to yield values of surface-tension of a surface at different intervals of time, not only without actually breaking the surface but also without disturbing the surface to any considerable extent.

Experimental Arrangement and Procedure

To obtain accurate and satisfactory results it is necessary to have a balance, in which the weights required to counterbalance the force of surface-

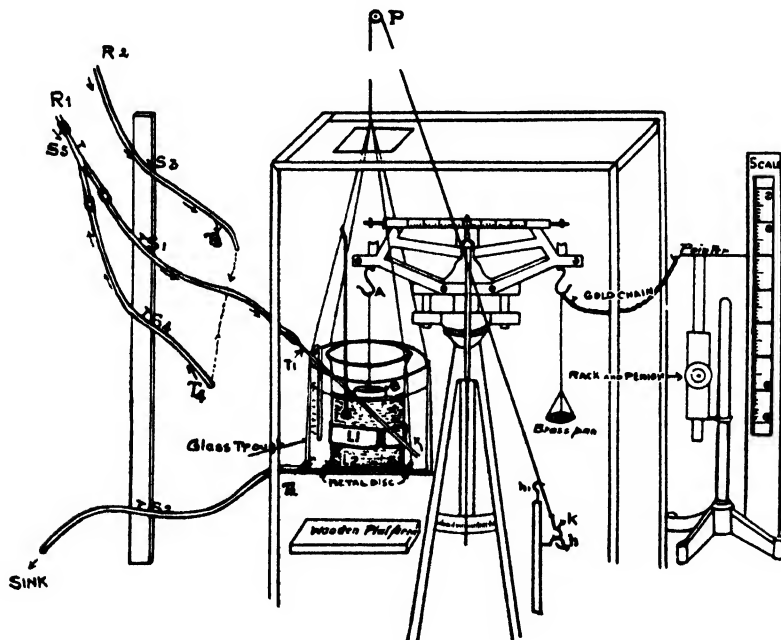


FIG. 1

tension would be continuously but very slowly increased. From one end of the balance-beam, (Fig. 1) was therefore hung a fine gold-chain; the other end of this chain was fastened to a vertical rod which could be moved up and down by means of a rack and pinion arrangement. A pointer attached to this vertical rod reads off its position against a vertical scale. The weight required to counterbalance the chain in different positions, was determined. The balance-pan at 'A' was replaced by an exactly circular flat basin 'B' made of thin nickel plate. Suspension was effected by means of a copper rod soldered to the centre of the plate. The basin was so made that the lower rim which was to touch the liquid surface, lay exactly in a horizontal plane when suspended from the hook 'A.' From time to time, the nickel basin was suspended just over a perfectly horizontal plane surface to observe if the lower rim remained horizontal, and distortion, if any, was set right.

Change of temperature has a great influence upon the actual value of surface-tension of a liquid or a solution; and sometimes it is likely to happen

that the temperature of the room fluctuates more than 2°C during the course of the experiment extending over eight or nine hours. At room-temperature evaporation also takes place at a considerable rate from a liquid surface, whose level thus falls continuously. Hence it was absolutely necessary to devise some means by which the rate of evaporation could be very considerably reduced and the temperature of the solution of which the surface-tension was to be measured, could be kept fairly constant.

The solution for investigation was, therefore, kept at a temperature about 5°C below that of the room by circulating cold water through a glass trough in which the beaker containing the solution whose surface-tension is to be determined, was immersed. The temperature as well as the level of the water surface in the outer trough were kept constant by carefully regulating the flow of cold water by means of screw-clips S_1 and S_2 . A lead plate L_1 was fixed round the beaker and another, L_2 interposed between the beaker and the glass-trough to avoid movement of the former in the trough.

As it is neither possible nor safe to handle the whole trough, with a view to bring the solution in the beaker just beneath the inverted basin, a suspending arrangement was taken recourse to; and when pulled by the end K of the string, the trough as a whole (as in the cut) could be raised up to the desired level and kept fixed by means of the hook h.

After raising the beaker to its proper position, the balance-beam was freed from arrestment and when oscillation had ceased, the solution was poured in by means of a pipette and the beam brought to arrestment. This procedure was repeated until the lower rim of the basin completely touched the surface of the solution. Weight was then added to the small pan on one end of the beam till it was a little less than that required to counterbalance the weight of the basin and the force of surface-tension at the other side. The final addition of weight was made by lowering the chain. The pointer of the balance remains almost motionless until a critical weight has been added, when it begins to move to the left, indicating that the weight has counter-balanced the force of surface-tension and the weight of the basin. The motion is slow and the ring is not suddenly torn off the surface of the solution. The weight on the pan and the position of the chain,—as indicated against the pointer,—in the vertical scale, were recorded. When the pointer was just moving towards the left, the beam was brought to arrestment, to prevent the basin from being torn off the surface, and the weight was slightly diminished by raising the chain. The surface-tension was thus measured without actually breaking the surface and with the minimum disturbance of the molecular arrangement of the surface.

All the precautions necessary for obtaining accurate results, were taken. For example, conductivity-water was always used, the glass vessels and the nickel basin were washed alternately with dilute acid and alkali, finally with conductivity water, and the basin was dried inside a desiccator containing "Sulphuric Acid." Kahlbaum's pure substances were used in every case.

Theoretical

(a) The surface-tension was calculated as follows:—

$$\text{Surface-tension of the solution} = \partial \times W_2/W_1$$

where ∂ = Surface-tension of water at the temperature of the experiment.

W_2 = Additional weight required to raise the basin from the surface of the solution while just touching.

W_1 = Additional weight required to raise the basin from the surface of pure water.

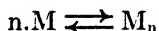
In the case of aqueous solutions of some substances, the surface-tension diminished with time, attaining a constant value after some four or five hours.

(b) General classification of solutions:—

On the basis of the experimental results recorded here and from the previous work in this laboratory, it is possible to classify solutions in three types:—

Type A:—True solutions of simple molecules whose velocity of diffusion is fairly large, and the equilibrium-concentration at the surface is reached too quickly to be detected by this method of measuring surface tension.

Type B:—Solutions consisting mostly of multi-molecular aggregates having small velocities of diffusion. In such a solution we may consider that an equilibrium exists between the large multimolecular aggregates and the simple molecules thus



where M represents simple primary molecules and M_n the molecular aggregates. When the solute exists mostly as multimolecular aggregates, the concentration of simple primary molecules is given by $C^{1/n}$ where C is the stoichiometric concentration. We assume that these simple molecules can only move up to the surface from the bulk of the solution. In the case of such a solution, on the air-liquid interface there is a competition for places on the surface between the solute and the solvent molecules. The kinetics of the formation of a solute film on this interface may be developed as follows:

The rate of diffusion of the solute molecules from the bulk of the solution into unit area of the surface may be considered to be proportional to the concentration of the simple solute molecules i.e. C . Now only a fraction of these solute molecules can condense on the surface. Those solute molecules which diffuse into the parts of the surface which are already covered with the solute are all reflected back. If at any time, x be the surface concentration of the solute molecule, and B be the area of the surface actually occupied by each solute molecule, then the uncovered surface per unit area is $1 - Bx$. The rate of condensation of solute molecules on the surface is therefore

$$= K_1 C^{1/n} \cdot \alpha (1 - Bx) \quad (1)$$

where α is the accommodation coefficient. It is probable that the smaller number of places held on the surface by the solvent molecules, the more tenaciously will those places be held by them, and therefore the accommo-

dation coefficient will diminish as the fraction of the surface covered by the solvent molecule diminishes.

$$\text{or} \quad \alpha = K_2 (1 - Bx)$$

Rate of condensation of solute molecules from the bulk of solution on the surface is given by

$$K \cdot C^{1/n} \cdot (1 - Bx)^2 \quad (2)$$

The rate of removal of solute molecules from the surface to the bulk of the solution is given by

$$X/T_1 \quad (3)$$

where T_1 is the average length of life of the solute molecules on the surface. If there are no forces of lateral cohesion between the solute molecules on the surface film, the value of T_1 remains constant for all surface concentrations of the solute at the same temperature. But, as a rule, it happens, that the forces of lateral cohesion have considerable magnitude and these forces will increase as the surface concentration of the solute molecules increases, or as the fraction of the unit area occupied by the solvent molecules diminishes. We may reasonably assume that

$$\frac{\Delta T + T_0}{T_0} = \frac{1}{1 - Bx}$$

where T_0 is the average life when the surface concentration of solute is very small and ΔT is the increment in the average life when the surface concentration is x . Hence rate of removal of solute molecules into the bulk of the solution is given by

$$K'x (1 - Bx) \quad (4)$$

Therefore the rate of increase of surface concentration

$$dx/dt = K C^{1/n} (1 - Bx)^2 - K'x (1 - Bx) \quad (5)$$

$$\text{or} \quad \frac{1}{(1 - Bx)^2} \frac{dx}{dt} = K C^{1/n} - \frac{K'x}{1 - Bx}$$

$$\text{or} \quad \frac{d \frac{x}{1 - Bx}}{dt} = K C^{1/n} - K' \frac{x}{1 - Bx} \quad (6)$$

when equilibrium has been attained

$$K C^{1/n} = K' \frac{x_{t_\infty}}{1 - Bx_{t_\infty}} \quad (7)$$

Now, as is well known, the gas laws may be applied to the unimolecular surface layer, and a general equation

$$F (A - B) = iRT \quad (8)$$

true for all solutions, may be obtained by combining the equation of Volmer¹

¹ Z. physik. Chem., 115, 255 (1925).

$$F(A - B) = RT$$

and the Bancroft equation¹

$$F - A = iRT,$$

F = the two dimensional gas pressure = $\sigma_{\text{solvent}} - \sigma_{\text{solution}}$

$A = 1/x$; B is the area actually occupied by a molecule

$$\text{or } F = \frac{iRT}{\frac{1}{x} - B} = iRT \frac{x}{1 - Bx} \quad (9)$$

Combining (9) with (6) we obtain

$$\begin{aligned} \frac{1}{iRT} \cdot \frac{dF}{dt} &= K C^{1/n} = K' F \\ &= K' \frac{x_{t_\alpha}}{1 - Bx_{t_\alpha}} = K' F \\ &= K' F_{t_\alpha} - K' F \end{aligned} \quad (10)$$

$$\text{or } dF/dt = iRT K' [F_{t_\alpha} - F]$$

$$\text{or } 2.3 \log_{10} \frac{F_{t_\alpha} - F_{t_1}}{F_{t_\alpha} - F_{t_2}} = K_1 [t_2 - t_1] = 2.3 \log_{10} \frac{\sigma_{t_1} - \sigma_{t_\alpha}}{\sigma_{t_2} - \sigma_{t_\alpha}} \quad (11)$$

$$\text{where } K_2 = iRT K' = \frac{iRT \cdot K \cdot C^{1/n}}{F_{t_\alpha}}$$

and σ_{t_1} , σ_{t_2} and σ_{t_α} are the surface tensions of the solution at times t_1 , t_2 and α .

σ_{t_α} is the value of surface tension obtained by extrapolation from graphs giving the variation of surface tension with time.

The values of K_1 as calculated between 1 and 2, 1 and 3, 1 and 4, 1 and 5 and so on are shown in tables in the experimental results. It will be noticed that for each substance the value of K_1 is practically constant for each experiment. K_1 also does not vary much with dilution indicating that $C^{1/n}/F_{t_\alpha}$ is approximately constant.

Solutes belonging to type B are therefore, intermediate between truly crystalloidal and completely colloidal solutions.

Type C:—Colloidal solutions:—

Du Noüy has observed a continuous logarithmic diminution of surface tension of normal rabbit serum solutions with time. The measurements were made by means of his tensiometer and extended over a period of two hours. In the case of sodium oleate solutions he found a very rapid drop of surface tension in the course of ten minutes. During this period, the rate of diminution of surface tension with time had a constant value. According to him, the surface tension of sodium oleate solution remains practically stationary after fifteen minutes. In our experiments the surface tension was first measured about five minutes after the solution had been poured in the

¹ J. Phys. Chem., 31, 1504 (1917).

measuring vessel, and then a series of readings were taken at intervals of about an hour. We have found in the case of the colloidal solutions that we have studied, that the variation of surface tension with time is not regular—maximum and minimum being often observed.

It is also interesting to note that Teague and Buxton¹ have classified the dyestuffs into three similar divisions as a result of dialysing experiments.

- (1) Schwach colloidal—of which methylene-blue is a representative.
- (2) Mässig and höch colloidal—e.g. neutral red, which cannot be dialysed at room-temp. but is very quickly dialysed at 37°C.
- (3) Vollständig colloidal—e.g. Congo-red.

Our classification is more or less similar to this, though the border lines between the different types are somewhat different.

Experimental Results

Type A:—Table I shows the results obtained for the surface tension of pure water and aqueous solutions of some substances of Type A, investigated at various time “*t*” (in minutes) reckoned from the time at which the first observation was made. The value of surface tension of solutions cannot be determined just at the moment a fresh surface is created. Hence the value of surface-tension given against the time “0” is the initial value obtained in every case.

TABLE I

Substance and temperature	Conc. in gr. mols. per litre	t_1	σ_{t_1}	t_2	σ_{t_2}
1. Water 21°C.	—	0	72.36	185	72.36
2. Fuchsine red 21°C.	.001	0	72.43	129	72.41
3. Salicylic acid 21°C.	.01 .02	0 0	60.64 59.25	281 252	60.50 59.02
4. Alizarin in caustic soda 21°C.	.0005 .001	0 0	72.31 71.40	231 285	72.47 71.30

Type B:—

Behaviour of solutions falling under the type B are recorded in Table II.

The significance of this value of “K,” has already been explained; the limiting values of surface tension σ_{t_∞} were obtained by extrapolation.

Type C:—

Peculiarities were observed while studying the aqueous solutions of Congo red. It is a lyophylic sol and does not dialyse through dialysing

¹ Z. physik. Chem., 60, 479 (1907).

TABLE II

Substance and temp.	Conc. in gr. mols per litre	t ₁	σ _{t1}	t ₂	σ _{t2}	t ₃	σ _{t3}	t ₄	σ _{t4}	σ _{t∞}	K _{t-2}	K _{t-3}	K _{t-4}	Mean K
Rhodamine B 20°C	.00063	0	60.34	39	59.05	135	57.06	225	55.63	54.50	.0064	.0061	.0072	.0064
	.001	0	52.23	36	51.29	109	49.75	188	48.84	47.80	.0066	.0075	.0071	.0070
	.0021	0	52.7	123	49.48	211	48.0	250	47.52	46.50	.0062	.0068	.0067	.0066
	.004	0	50.86	115	46.49	213	45.08	266	44.54	43.60	.0079	.0074	.0076	.0076
	.0065	0	49.21	103	44.91	218	42.99	378	42.02	41.50	.0079	.0075	.0072	.0075
Eosine yellowish 17°C	.002	0	71.89	69	70.38	136	69.34	241	68.21	65.15	.0036	.0034	.0038	.0036
	.01	0	65.13	74	63.90	147	62.83	240	62.05	59.81	.0035	.0038	.0036	.0036
	.03	0	62.66	60	61.33	190	60.38	300	59.68	57.85	.0042	.0033	.0032	.0036
	.05	0	60.78	180	57.85	253	57.34	344	56.82	55.80	.0040	.0037	.0035	.0037
	.0025	0	49.14	38	48.08	76	47.38	145	46.51	46.0	.0107	.0107	.0125	.013
α-Naphtholsulphonic acid 21°C	.01	0	46.90	63	44.17	148	42.74	244	41.74	40.85	.0094	.0096	.0099	.0096
	.05	0	41.48	66	38.05	138	36.40	207	35.66	34.80	.0109	.0102	.0099	.0103
	.001	0	64.86	72	63.10	183	61.40	282	60.40	58.50	.0044	.0042	.0040	.0042
B-Naphthylamine disulphonic acid 21°C	.005	0	51.97	37	51.40	103	50.53	180	49.61	47.40	.0040	.0036	.0040	.0039
	.016	0	49.61	114	47.38	188	46.87	267	46.40	43.0	.0031	.0030	.0033	.0031
	.014	0	67.08	103	64.75	246	63.12	324	62.21	60.8	.0044	.0040	.0046	.0043
Di-methyl p-phenylene diamine hydrochloride 24°C	.02	0	66.54	103	53.81	186	62.11	338	60.95	59.0	.0043	.0047	.0040	.0043
	.025	0	64.65	34	63.78	103	62.62	185	61.57	58.5	.0044	.0040	.0041	.0042

TABLE II (Continued)

Substance and temp.	Conc. in gr. mols per litre	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}	σ_{t_x}	K_{1-2}	K_{1-3}	K_{1-4}	Mean K
Dioxybenzoic acid 24°C	.0071	0	66.68	33	65.31	113	64.87	182	64.01	63.0	.0087	.0081	.0088	.0085
	.0224	0	58.03	66	57.0	134	56.16	207	55.66	55.5	.0083	.0080	.0081	.0081
	.049	0	56.37	70	54.90	135	54.23	233	53.44	52.9	.0089	.0075	.0079	.0081
α -naphthylamine hydrochloride 21°C	.005	0	55.54	108	52.84	219	51.37	291	50.85	49.65	.0056	.0056	.0050	.0054
	.007	0	51.70	73	50.00	175	48.78	210	48.27	47.0	.0059	.0057	.0059	.0058
	.0121	0	48.38	74	46.90	195	45.47	266	45.14	44.1	.0055	.0057	.0052	.0055
β -naphtholsulphonic acid 21°C	.0025	0	63.88	67	61.58	174	59.33	290	58.60	55.5	.0036	.0032	—	.0034
	.005	0	59.41	113	58.01	188	57.41	284	56.68	54.9	.0033	.0032	—	.0033
	.05	0	51.39	67	49.99	139	49.02	209	48.59	45	.0039	.0036	.0030	.0035
Aniline hydrochloride 24°C	.0018	0	70.37	112	69.16	255	67.98	449	66.71	66.30	.0029	.0031	—	.0030
	.0027	0	70.33	106	69.0	250	67.54	356	66.60	65.0	.0027	.0029	—	.0028
	.0939	0	64.75	131	60.85	198	59.56	266	58.76	52.60	.0026	.0029	—	.0028
Chinolin yellow 18°C	.0103	0	72.51	83	70.01	150	69.16	225	68.57	68.26	.0106	.0103	.0115	.0108
	2.56%	0	66.77	76	65.72	127	65.48	197	65.27	65.07	.0118	.0107	.0095	.0106
	5.8%	0	65.86	93	63.25	132	62.88	200	62.43	62.03	.0112	.0113	.0101	.0109
about 6% (saturated)		0	64.92	73	63.16	229	62.16	273	62.03	61.86	.0116	.010	.0106	.0107

TABLE II (Continued)

Substance and temp.	Conc. in gr. mols per litre	t ₁	σ _{t₁}	t ₂	σ _{t₂}	t ₃	σ _{t₃}	t ₄	σ _{t₄}	σ _{t_∞}	K ₁₋₂	K ₁₋₃	K ₁₋₄	Mean K
Biebrich scarlet 18°C	.0005	0	68.37	85	67.30	139	66.89	190	66.59	66.55	.0104	.0113	—	.0108
	.00093	0	65.31	190	64.19	206	64.12	228	64.06	63.95	.0091	.010	.0110	.0105
	.0031	0	59.24	117	57.42	171	57.16	207	57.06	56.84	.0101	.0117	.0115	.0111
Benzo-purpurin 17°C	.001	0	64.31	39	63.08	67	62.47	180	61.38	60.88	.0113	.0114	.0107	.0111
	.0021	0	62.29	70	59.96	136	59.09	212	58.57	58.12	.0116	.0107	.0105	.0109
	.008	0	57.95	39	57.36	140	56.69	178	56.52	56.27	.0110	.010	.0107	.0106
Victoria yellow 17°C	.001	0	63.62	39	62.24	58	61.99	80	61.80	61.34	.0237	.0216	.0200	.0217
	.002	0	58.38	89	57.12	122	57.03	—	—	56.95	.023	.023	—	.023
	.003	0	55.42	36	54.28	61	54.0	136	53.64	53.45	.023	.0209	—	.0219
Aniline orange (G.G.) 20°C	.003	0	70.87	76	67.78	145	66.79	218	66.12	65.80	.0123	.0113	.0111	.0115
	.006	0	65.69	34	64.60	101	63.36	175	62.75	62.29	.0113	.0114	.0109	.0112
	.010	0	64.85	62	60.88	168	58.61	230	57.72	57.15	.0116	.010	.0112	.0109
Chrysoidine crystal 17°C	.0005	0	61.48	62	56.65	129	54.78	235	53.56	52.75	.0127	.0111	.010	.0113
	.001	0	55.04	63	53.02	132	51.94	170	51.72	51.24	.0120	.0120	.0121	.0120
	.00199	0	54.69	38	52.95	94	51.68	175	50.68	50.0	.0121	.0108	.0110	.0113
Brilliant green (very dilute solution only)	.0005	0	63.46	71	59.46	147	57.82	216	57.15	56.0	.0115	.0109	.117	.0114

membranes.¹ After reaching a minimum value, the surface-tension increases rapidly, comes to a maximum and a fall for the second time ensues, thus causing the curve to show the variation of surface-tension with time to be an irregular one. The steepness of the curves increases with rise of concentration. Table III will make the points clear.

It is interesting to note that the aqueous solution of brilliant green falls under Type B, only when the dilution is very great. It behaves as a colloidal solution (as will be seen in Table IV) when the concentration increases.

TABLE III

Substance and Temp.	Conc. in gr. mols.	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}
Congo red 20°C.	(1) .0022	0	71.78	69	68.60	189	67.78	240	67.41
	(2) .0051	0	69.95	79	66.97	205	67.08	303	67.74
	(3) .0102	0	68.11	108	63.95	137	63.90	235	64.12
	* (4) .0051	0	65.89	68	63.88	121	63.13	240	62.75
Brilliant green 21°C.	(1) .00081	0	60.19	61	58.05	102	57.54	162	57.68
	(2) .00201	0	53.76	77	52.12	109	52.42	187	54.43
	(3) .004	0	53.26	45	53.07	111	59.98	218	60.42
	** (4) .004	0	56.02	132	53.70	208	53.32	364	53.75

* Results obtained on studying the solution (2) after it was kept for about a month, are shown in (4). The values of surface-tension as well as the nature of its variation with time is found to be changed.

** When studied after keeping the solution (3) for about a month.

TABLE IV

Temp.	Substance and Conc.	t_1	σ_{t_1}	t_2	σ_{t_2}	t_3	σ_{t_3}	t_4	σ_{t_4}
21°C	Fuchsine red (.008)	0	71.78	32	71.76	85	71.74	125	71.76
21°C	Fuchsine red (.008) in .014 N. KCl solution	0	70.66	21	70.88	67	70.37	101	70.79
21°C	Fuchsine red in .032 N. KCl solution (.008)	0	66.55	20	65.55	76	66.77	120	67.53
21°C	Fuchsine red in .06 N. KCl solution (.008)	0	63.30	61	61.81	140	62.23	239	64.94
21°C	When KCl soln. added in excess (i.e. sufficient to precipitate the colloid)	0	72.23	16	72.23	90	72.25	125	72.25

¹ Z. physik. Chem., 60, 479 (1907).

We have seen at the very beginning that the aqueous solution of fuchsine red shows no variation of surface-tension with time. (Table I.)

The addition of an electrolyte, such as potassium chloride or sodium chloride, to a true solution of fuchsine red renders it colloidal. It is therefore to be expected that a true solution of fuchsine red belonging to type A, will on addition of potassium chloride in quantities not large enough for coagulation begin to behave as a solution of type C. This has been actually observed, as will be seen in Table IV.

As will be seen in Table IV, the addition of increasing quantities of potassium chloride transforms a solution of fuchsine red from Type A to Type C through solutions of Type B.

The classification of solutions into three classes based on experiments on variation of surface tension with time has been corroborated, at least qualitatively, by dialysing experiments. The results are given in (Table V).

TABLE V

		Remarks
1. Substances dialysing very rapidly through collodion membranes at 27°C (e.g. of the type potassium chloride):—	I. Fuchsine red II. Methylene blue	Solutions of Type A—molecularly dispersed
2. Dialysing rapidly at 27°C:—	I. Victoria yellow II. Biebrich scarlet III. Aniline orange (G.G.) IV. Rhodamine B V. Crystal violet VI. Chrysoidine cryst.	Solutions of Type B—consisting mostly of small molecular aggregates in equilibrium with very low conc. of simple molecules
3. Dialysing slowly at 27°C:—	I. Brilliant green	Solutions of Type C colloidal solutions
4. Dialysing very slowly at 27°C, but somewhat rapidly at 60°C:—	I. Benzo purpurin*	containing scarcely any simple molecule
5. Dialysing not even at 60°C:—	I. Congo red	"

* Kraft classified benzopurpurin with congo red, as neither of the two was found to dialyse through parchment paper.

Our thanks are due to Mr. S. K. Sarkar for help in carrying out some of these experiments.

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CHANGES IN PHYSICAL AND ELECTRICAL PROPERTIES OF A MINERAL INSULATING OIL, HEATED IN CONTACT WITH AIR *

BY HUBERT H. RACE

I. Object

To obtain a clearer insight into the changes in a mineral insulating oil resulting from heating in contact with air, the following properties were studied in portions of the same oil which had been oxidized under different conditions.

- A. D-C. conductivity at 115°C.
- B. Dielectric losses at 30°C. for frequencies between 10^3 and 10^6 cycles per second.
- C. Oil spreading on water using Langmuir's method.
- D. Ultramicroscope particle count.
- E. Viscosity using modified Ostwald viscometer.
- F. Refractive index using a Pulfrich refractometer.
- G. Acid number.

These chemical, physical and electrical tests were all made on the same samples so as to correlate the results of the different types of measurement and determine whether sensitive electrical equipment could be advantageously used to supplement the usual chemical and physical tests.

II. Preparation of Samples

TABLE I

Physical Data for No. 5317 Oil

(1) Flash Point	225°C.
(2) Fire Point	265°C.
(3) Acid value	4×10^{-5} grams KOH per grams of oil
(4) Density at 30°C.	0.935 grams per cc.
(5) Viscosity at 30°C.	10 poises

A portion of commercial cable oil having the general characteristics shown in Table I was divided into nine equal samples which were aged in contact with air in a G. E. Life Test oven according to the schedule shown in the first three columns of Table II. This procedure was used so that the results could be interpreted directly in terms of standard practice in the Cable Plant where resistivity measurements before and after heating 96 hours at 115°C. are used

* This paper is based in part upon data presented at the fourth annual conference of the committee on electrical insulation, division of engineering and industrial research, National Research Council, held at Harvard University, Cambridge, Mass., Nov. 13-14, 1931. See Elec. Engineering, 51, 33 (1932).

in factory control. The time schedule for heating at the different temperatures was chosen so that corresponding samples at the different temperatures would show approximately the same change in conductivity. This was estimated from preliminary data on changes in conductivity with heating temperature.

III. Experimental Procedure and Data

A.—D. C. Conductivity at 115°C.

About two years ago the small oil conductivity testing set shown in Fig. 1 was developed for measuring the direct current conductivity of insulating oils. The wiring diagram for this set is shown in Fig. 2. Its main advantages are ease of operation and good control of the temperature of the sample under test. The extremely good electrical properties of these insulating oils require special care in the design of the testing cell. Fig. 3 shows such a cell, made of stainless steel



FIG. 1
Oil Resistivity Testing Set

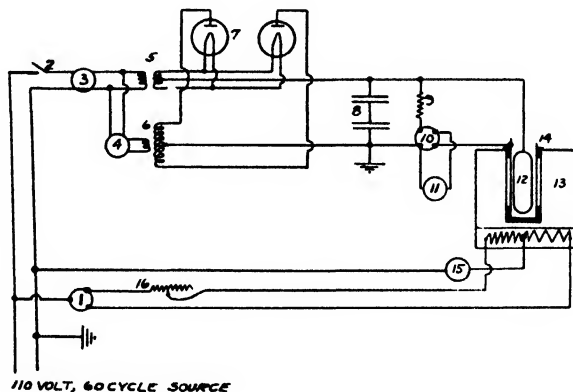


FIG. 2
Wiring Diagram

1. Two-circuit Heater Switch
2. Safety Switches in Doors.
3. Transformer Switch.
4. Ten-second delay Relay.
5. Filament Transformer Y 2006.
6. Plate Transformer UP 1016.
7. Two Mercury Rectifier Tubes—PJ 28.
8. Two 800 volt, 1 microfarad Capacitors.
9. 10^6 -ohm wire wound Resistor.
10. Special Galvanometer Switch.
11. Portable Insulation Testing Galvanometer.
12. Quartz insulated Oil Testing Cell.
13. Heater (not used when a cell is placed on an oil storage tank).
14. Textolite insulation between Cell and Heater.
15. Thermostat for controlling Heater (not necessary).
16. Variable Resistance for low Heat Control.

TABLE II

Summary of Experimental Results obtained by heating No. 5317 Oil in
Contact with Air

Sample No.	A		B		C		D		E		F	
	Conductivity at 115°C.		Max. loss		Spreading		Particle count		Viscosity		Index of	
	Oxidation Time hours	Temp. °C.	γ mho. per cm. cube $\times 10^{-12}$	Factor ϵ''_m (nu- meric)	Area A_o Sq. cm. per gram of oil $\times 10^3$		First	Second	at 30°C. η poises		Refraction at 30°C. (r) (numeric)	
1	4	115	1.02	2.11	3.3		4	139	10.7		1.5098	
2	28	"	2.62	2.20	12.0		5	56	10.4		1.5098	
3	96	"	11.8	2.74	26.0		33	51	10.0		1.5102	
4	2	130	0.84	2.15	3.4		67	253	9.7		1.5101	
5	14	"	2.17	2.26	6.7		89	41	11.0		1.5095	
6	48	"	8.35	2.6	22.0		166	45	10.7		1.5108	
7	1	150	0.75	2.15	3.0		136	5	9.5		1.5108	
8	7	"	1.45	2.27	7.0		32	75	11.9		1.5110	
9	24	"	4.55	2.52	21.0		103	3	11.9		—	

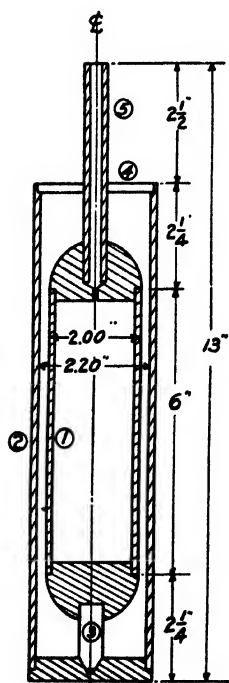


FIG. 3
Oil Resistivity Testing Cell

with fused quartz insulation. The inner electrode (1) is a hollow cylinder to which hemispherical ends have been welded using an atomic hydrogen flame. The bottom of the outer cylinder (2) has a central conical hole into which the fused quartz post (3) fits. This post is held by a friction fit in a central hole in (1) but it may be removed for cleaning. The top of the inner electrode is centered by a fused quartz collar (4) which is also made with a sliding fit so that the inner electrode may be easily removed for cleaning. The small cylinder (5) serves as a high lead to the cell, as the top centering post and as a container for a thermometer to indicate the temperature of the inner electrode. The major advantages of this cell are as follows:

- It is made of materials which are not attacked by the oil and do not act as catalysts on the oil.
- It is easily taken apart for cleaning, and
- Its calibration remains constant even though it is repeatedly taken apart for cleaning.

With the above equipment the conductivity of each sample was determined at 115°C., as is shown in Table II. The curves in Fig. 4, plotted from these data, indicate that, *the longer the aging time, the greater is the effect of high temperature on the conductivity.*

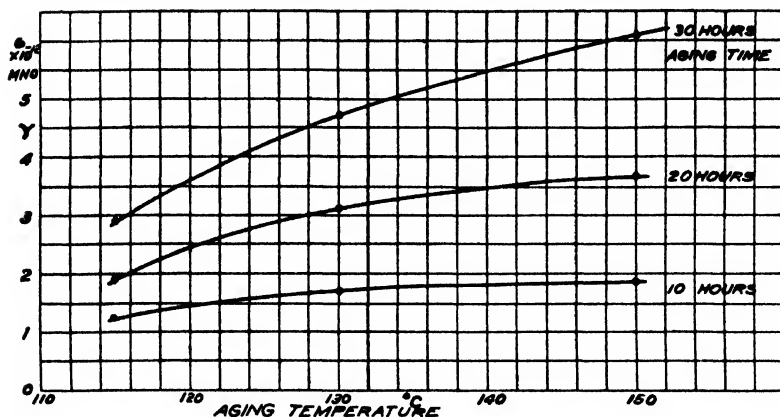


FIG. 4

Variation of Conductivity resulting from heating
5317 Oil in Air at different Temperatures

B.—High Frequency Measurements of Electrical Properties.

Previous work on the high frequency electrical properties of insulating oils has suggested the presence of polar molecules in oil and the possibility of estimating their size.^{1,2}

It has been found convenient to interpret the high frequency measurements in terms of the equivalent parallel circuit shown in Fig. 5. The com-

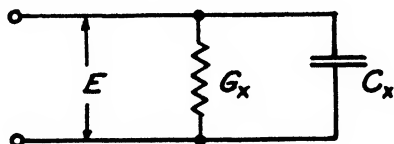


FIG. 5

Parallel circuit electrically equivalent to Sample

plex expression for the reciprocal impedance of the measuring circuit is given by the relation

$$Z^{-1} = G_x + i\omega C_x = \omega C_v (\epsilon'' + i\epsilon') \quad (1)$$

in which

G_x = the equivalent parallel conductance of the sample

C_x = the equivalent parallel capacitance of the sample

ω = $2\pi f$, where f = electrical frequency in cycles per second

i = $\sqrt{-1}$

C_v = capacitance of the same geometric arrangement of electrodes in vacuum.

¹ D. W. Kitchen and Hans Muller: *Phys. Rev.*, (2) **32**, 979 (1928).

² H. H. Race: *Phys. Rev.*, (2) **37**, 430-446 (1931).

For comparative purposes it is convenient to study unit quantities which may be defined by comparing the two forms of equation (1) as follows:

$$\epsilon' = (C_x/C_v) = \text{capacitance factor* (Dielectric Constant)} \quad (2)$$

$$\epsilon'' = (G_x/\omega C_v) = \text{loss factor} \quad (3)$$

$$\sin \tan^{-1} (\epsilon''/\epsilon') = \text{power factor} \quad (4)$$

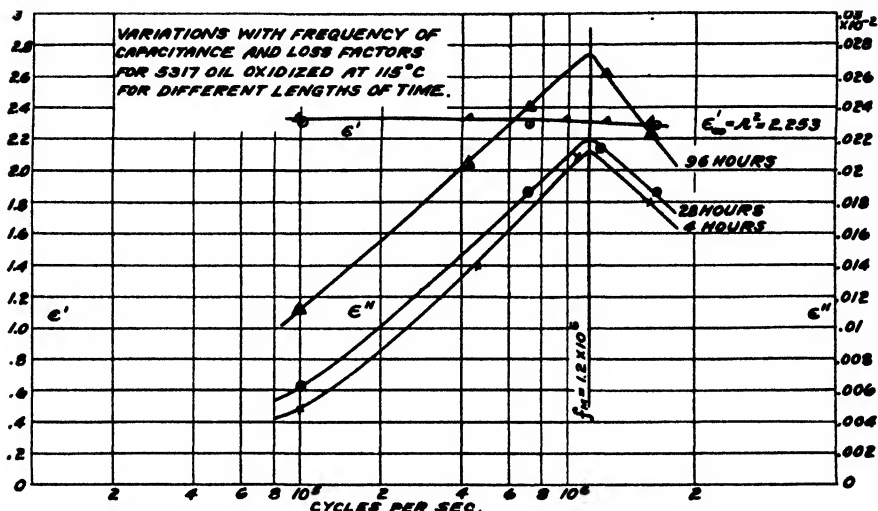


FIG. 6

Figs. 6, 7, and 8 show ϵ' and ϵ'' plotted against the logarithm of the frequency for the nine samples. The data have been presented in this way so that they may be studied in terms of Debye's theory of polar molecules.³ From this theory expressions can be derived for ϵ' and ϵ'' as functions of frequency and the general form of these relations is shown by Fig. 9. For these oils the change of ϵ' with frequency is small, therefore, to more clearly show the changes predicted by the theory, Fig. 9 has been plotted for an assumed condition such that the decrease in capacitance with increased frequency is 50%.

The conditions required by the theory for the frequency (f_m) at which the dielectric loss is a maximum are particularly interesting. At this frequency the particular values of the capacitance factor (dielectric constant) and the loss factor² can be shown to be

$$\epsilon'_m = \frac{1}{2} (\epsilon'_0 + \epsilon'_\infty) \quad (5)$$

$$\epsilon''_m = \frac{1}{2} (\epsilon'_0 - \epsilon'_\infty) \quad (6)$$

* This new name is suggested because ϵ' is not necessarily constant, but may vary with both frequency and temperature and because the word, *capacitance*, refers specifically to the reactive component whereas the word, *dielectric*, has a more general meaning. See Electrical Engineering, 51, 354 (1932).

³ P. Debye: "Polar Molecules" (1929).

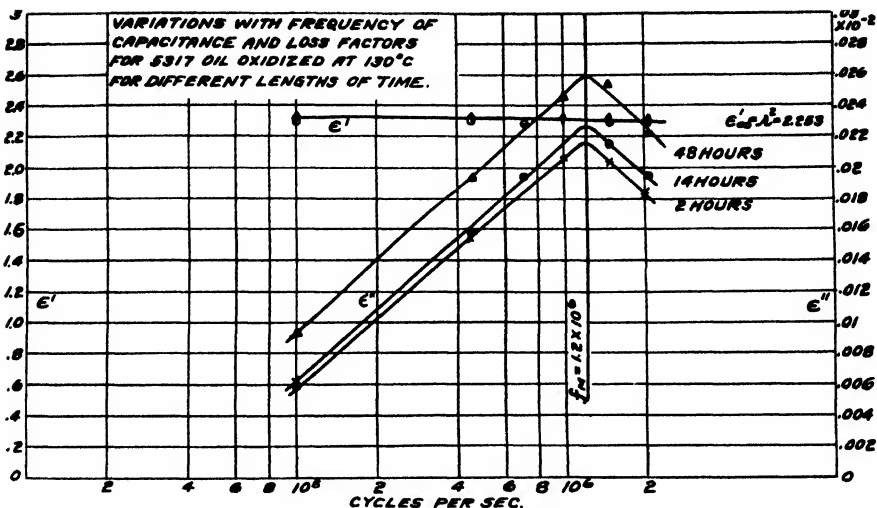


FIG. 7

where ϵ'_0 and ϵ'_∞ are respectively the capacitance factors (dielectric constants) at zero and infinite frequencies.

The curves in Figs. 6, 7, and 8 show small but definite decreases in ϵ' with increased frequency and are apparently approaching the limiting value $\epsilon'_\infty = 2.253$, which is the square of the measured index of refraction as required by theory.

The loss curves all have their maxima at the same frequency and show increasing loss with increasing oxidation. The maximum ordinate of the curve for ϵ'' should be calculable from the theory by eq. (6). For example the maximum ordinate of the 24 hour curve of Fig. 8 should be

$$\epsilon''_m = \frac{1}{2} (2.34 - 2.53) = .0435$$

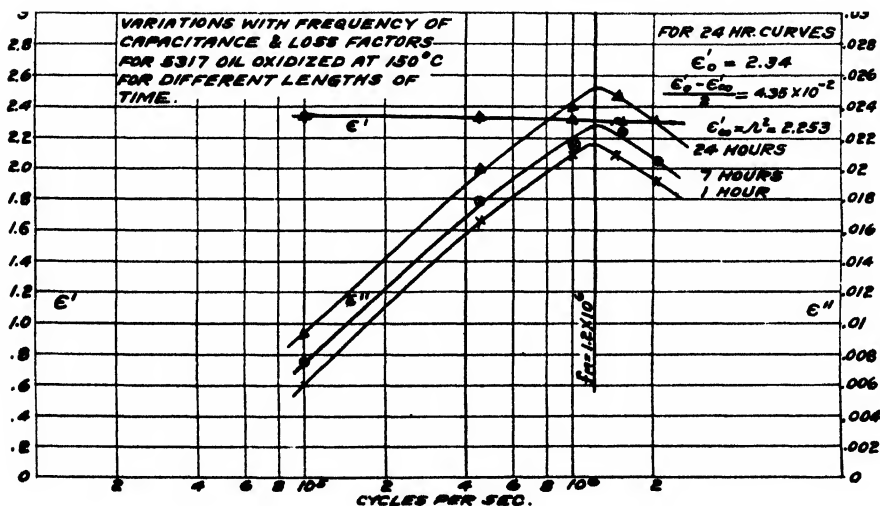


FIG. 8

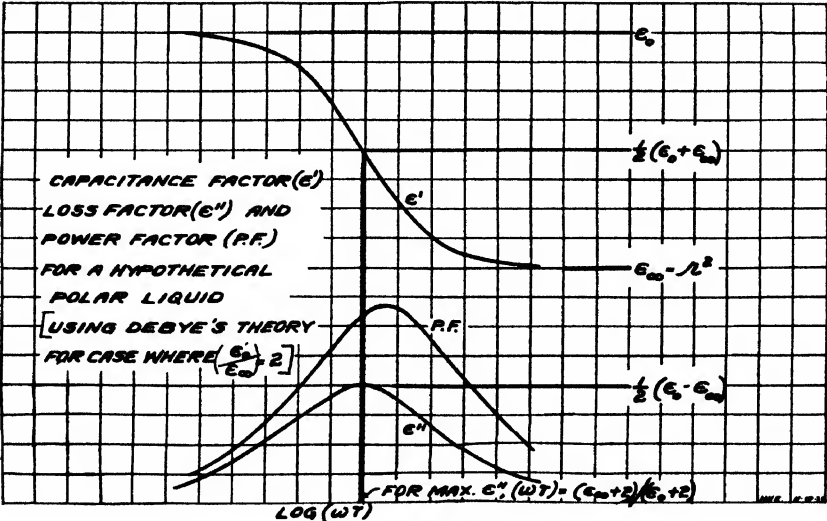


FIG. 9

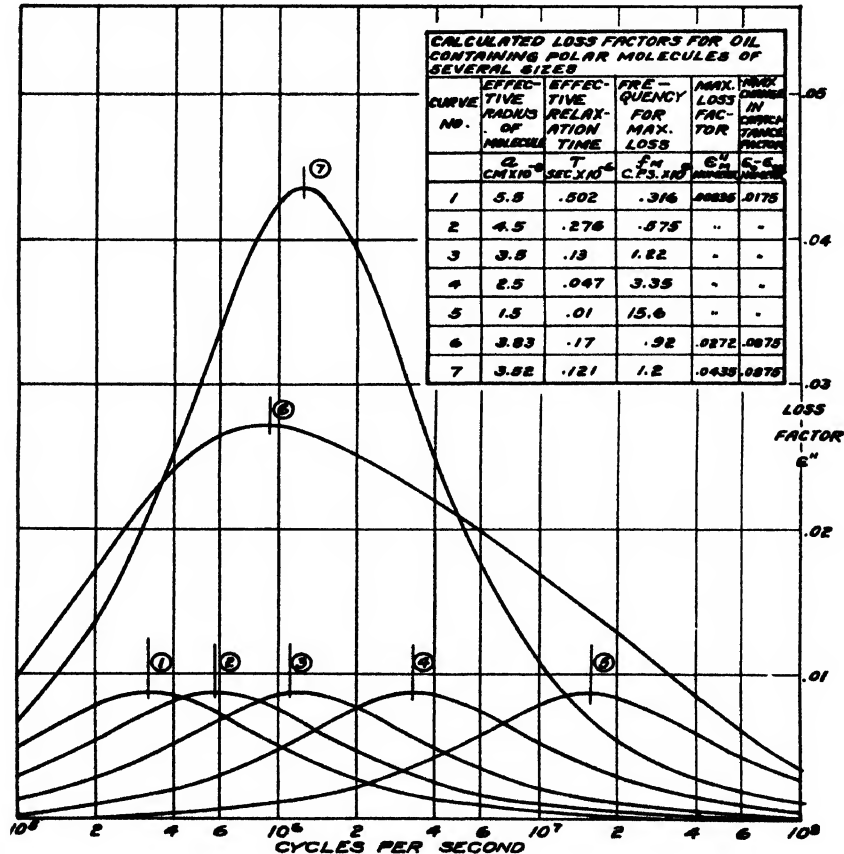


FIG. 10

The measured ϵ''_m is seen to be only .0253, however, a possible explanation for this difference is indicated in Fig. 10. Equation 7 is based upon the assumption that all observed effects result from the orientation of particles of one size only. If there are any polar molecules present, they are probably of several sizes. Then the change in ϵ' would represent the sum of the contributions of particles of all sizes, since at frequencies approaching zero they would all orient completely and at frequencies approaching infinity none of them would orient. The loss factors for the several sizes, however, would have their maxima at different frequencies since the relaxation time depends upon the size of particle. Therefore the sum of the loss curves would have a maximum ordinate considerably less than would have been obtained if the particles had been all of one size. For example, in Fig. 10 the total change in ϵ' has been assumed to result from the orientation of equal numbers of molecules of five different sizes (arbitrarily chosen). For this assumed illustration curve (6) shows that the maximum ordinate of the sum of the five loss curves is only about 62% of the maximum ordinate of curve (7) for which all the particles are assumed to be of one size only. The resulting ratio is nearly the same as that found between the observed and calculated values of ϵ''_m corresponding to the 24 hour curve of Fig. 8 and indicates the plausibility of this explanation for the difference between the observed and calculated values.

From Debye's theory the relaxation time (τ) of the polar molecules is given by the expression

$$\tau = \frac{1}{2\pi f_m} \left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) = \frac{4\pi\eta a^3}{kT} \quad (7)$$

where f_m = frequency at which maximum loss occurs

η = viscosity in poises

a = effective radius of the polar molecule in cm.

k = Boltzmann's constant = 1.37×10^{-16}

and T = absolute temperature

Using this relation, the effective size of the orienting particle can be obtained directly from the experimental measurements. For example from the 24-hour curve of Fig. 8,

$$a = \left[\left(\frac{1.37 \times 10^{-16} \times 303}{6.28 \times 1.2 \times 10^6 \times 12.56 \times 10} \right) \left(\frac{4.253}{4.34} \right) \right]^{1/3} = 3.4 \times 10^{-8} \text{ cm.}$$

The exactness of equation 7 may be questioned because it assumes the validity of Stokes' law of viscosity which may not be an accurate measure of the frictional coefficient for an orienting particle in a viscous medium. The calculated size of particle is considerably smaller than that expected for an oil molecule. For example Langmuir⁴ shows that the stearic acid molecule has an effective cross sectional area of 22×10^{-16} sq. cm. and a length of 25×10^{-8} cm. *This leads to the conclusion that the whole molecule does not rotate but*

⁴ I. Langmuir: J. Am. Chem. Soc., 39, 1848 (1917).

rather the polar group moves with reference to the rest of the molecules so that the radius calculated from the electrical measurements is a measure of the effective size of the portion of the molecule which is contributing to the polar movement.

C.—Oil spreading on Water.

The oil spreading measurements were made in order to obtain an independent check on the formation of polar molecules during oxidation and to confirm the approximate correlation observed by Shanklin and Mackay⁵

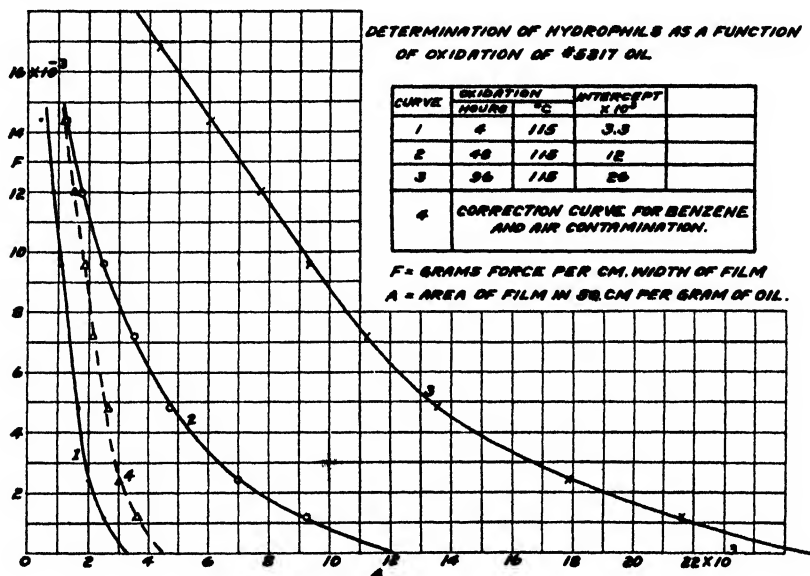


FIG. 11

between conductivity and hydrophil measurements. The tests were made using apparatus similar to that employed by Langmuir⁴ except for minor modifications and the results are shown in Figs. 11, 12, and 13. Each curve was obtained by increasing the compressive force applied to the film in definite steps and measuring the area covered by the film. These curves were then extrapolated to zero force in order to obtain the area of a monomolecular layer of the polar constituents of the oil on water. This area, A_0 , is then the measure of the hydrophil content per gram of oil.

Considerable care was necessary to minimize oil contamination. The benzene was purified by repeated redistillation and the apparatus was cleaned after every run. The magnitude of residual errors is indicated by curve (4) of Fig. 11 which illustrates the correction curve taken before each set of runs and subtracted from the observed readings. The residual errors account for more than 50% of the observed spreading for the least oxidized samples. For the most highly oxidized samples the errors are relatively small.

⁵ G. B. Shanklin and G. M. J. Mackay: A.I.E.E. Trans., 48, 364 (1929).

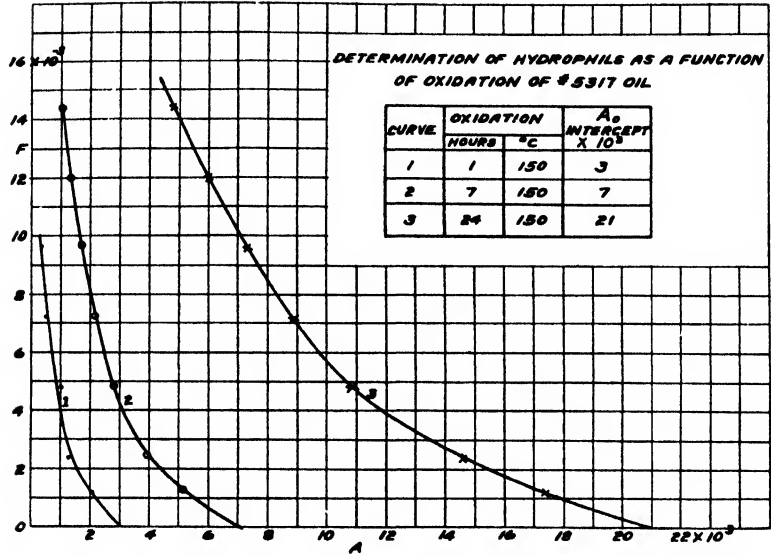


FIG. 12

The values of A_0 were plotted against aging time and points from these curves were replotted in Fig. 14 for direct comparison with corresponding curves showing changes in conductivity (Fig. 4). The trends of these two sets of curves are different and indicate that oxidation at higher temperatures has a greater effect in producing polar particles than in producing particles capable of carrying a charge.

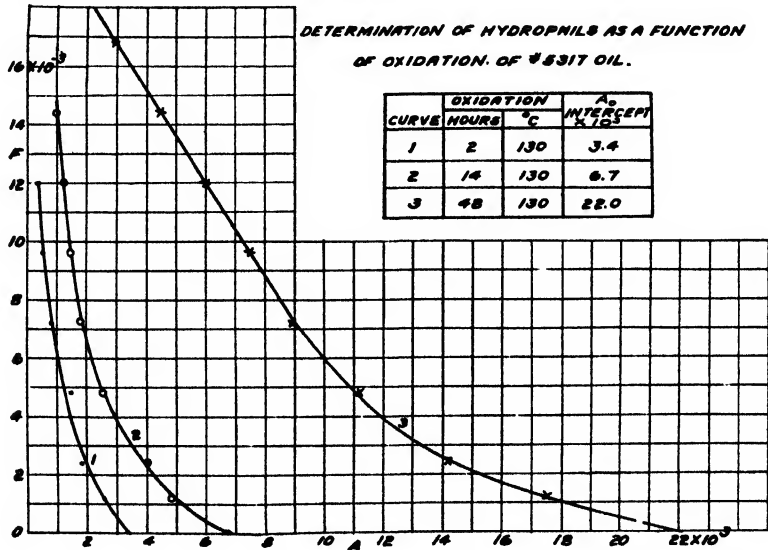


FIG. 13

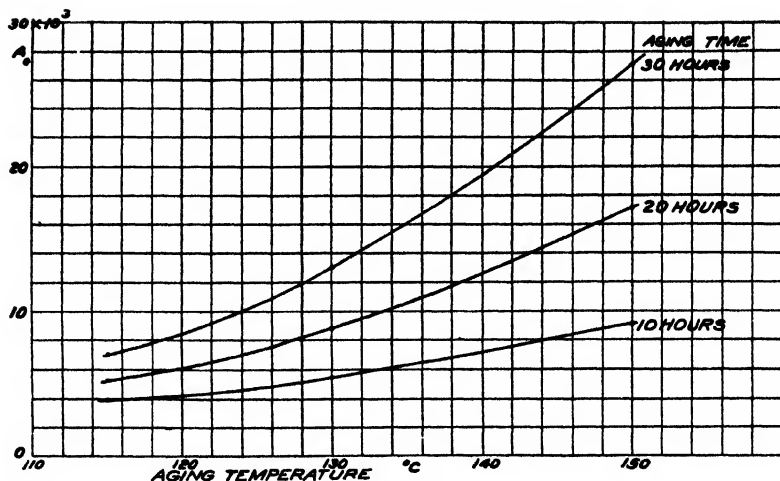


FIG. 14
Variation of Hydrophils produced by Heating 5317
Oil in Air at different Temperatures

A comparison between the maximum ordinate (ϵ''_m) of each curve of high frequency loss and the corresponding spreading area (A_0) on water is plotted in Fig. 15. This straight line relation is very interesting because it indicates that regardless of the temperature at which the oxidation occurred the increase in hydrophils was proportional to the increase in the number of polar particles responsible for the dielectric loss. The fact that this line does not pass through the origin can hardly be accounted for by experimental error. The apparent inference is that a large component of the loss is not caused by particles which spread on water. This means either that polar groups are formed which are not soluble in water or that there is some other

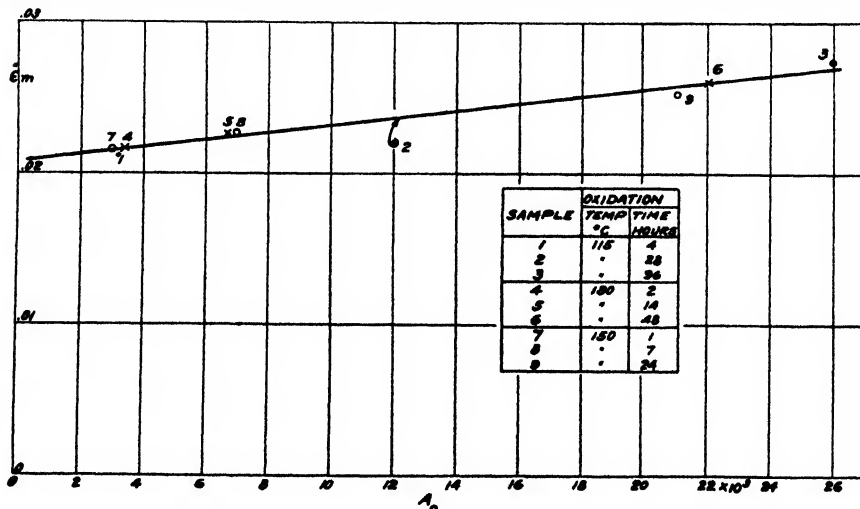


FIG. 15
Proportionality between Loss Factor and Hydrophils for 5317 Oil oxidized at
different Temperatures for different lengths of Time

loss mechanism having a maximum response at approximately the same frequency. Such a mechanism might be the relative translational motion of ions of opposite sign in colloidal interfaces or in ionic atmospheres although no experimental data are available to substantiate this suggestion.

It is possible that further experimental work along this line may show that the effects can be explained in terms of an ionic atmosphere such as Debye and Falkenhagen⁶ and Wien⁷ employ to explain conduction measurements in strong electrolytes at high frequencies and high gradients.

D.—*Ultramicroscope Particle Counts.*

Careful ultramicroscope particle counts were made on portions of these nine samples in another laboratory where facilities were available. Results from one set of samples were quite erratic so second portions of the same samples were forwarded for duplicate determinations. The investigators reported that filters were used because of fluorescence in the oil and that the results were subject to considerable error because of apparent local concentration of particles at different points in the samples. The high viscosity of the oil prevented rapid random distribution of the suspensoids. The results of the two sets of measurements are shown in Table II and indicate *either that the methods of sampling, shipping and counting introduced large errors or that the suspensoids large enough to be seen in the ultramicroscope were entirely unrelated to those causing changes by the other experiments.* It seems that the latter is more probable.

E. *Viscosity Measurements.*

The viscosity of each sample was determined with a modified Ostwald viscometer which had previously been calibrated and used for measuring the viscosity of insulating oils. The results of these measurements are also shown in Table II and indicate that *if oxidation caused any consistent change in viscosity, this change was smaller than the experimental error which was about 2%.*

F. *Index of Refraction Measurements.*

As one step in interpreting the high frequency measurements it was necessary to determine the index of refraction (r) since by Debye's theory $\epsilon'_{\infty} = r^2$. Each of the samples was measured in a Pulfrich refractometer at 30°C., using the red mercury (c) line and the results are recorded in Table II. *The observed differences were of the order of 0.1% indicating either a slight trend toward higher refractive index with greater oxidation or erratic differences of this order between samples.*

G. *Acid Number.*

After all the other measurements had been completed, the remaining portions of the samples were too small to make the usual check for acid number. However, since titration for acid number is one of the routine

⁶ P. Debye and H. Falkenhagen: *Physik. Z.*, **29**, 401-426 (1928).

⁷ M. Wien: *Ann. Physik*, **83**, 327-361 (1927).

measurements made on all cable oils, a considerable amount of data is available. Only small differences in acid number have been observed between samples before and after the usual 96 hour — 115°C. aging tests. An average acid value for a large number of tests is about 5×10^{-5} grams of KOH per gram of oil. This can be converted to an approximate oil-spreading area by assuming that the polar molecules have the same cross section and molecular weight as a stearic acid molecule. 1 g. of KOH combines with $\frac{284}{56} = 5.07$ g.

of stearic acid. Stearic acid contains $\frac{6.06 \times 10^{23}}{284} = 21.3 \times 10^{20}$ molecules per g. The cross section of stearic acid molecule = 22×10^{-16} sq. cm. Therefore $A_o = 5 \times 10^{-5} \times 5.07 \times 21.3 \times 10^{20} \times 22 \times 10^{-16}$ or $A_o = 1.19 \times 10^3$ sq. cm. per gram of oil.

This calculated area is considerably smaller than that observed for the three most highly oxidized samples. For example, the portion heated 96 hours at 115°C. showed a spreading area of $A_o = 26 \times 10^3$ sq. cm. per gram of oil. Thus the spreading for this sample was about 22 times greater than than calculated from the acid number. This difference indicates that *the acid number test is not suitable for detecting changes, produced by oxidation, of the polar constituents of an oil.*

IV. Conclusions

1. Oxidation considerably increases the ability of oil to spread on water, but corresponding changes in acid number are very small. For example, the measured spreading of sample 3 was twenty-two times greater than the value calculated from the acid number, indicating that the major proportion, if not all, of the non-volatile products containing polar groups could not be detected by the acid number test. This result may vary considerably with the type of oil used and emphasizes the value of the oil spreading measurements.

2. Oxidation increases the high-frequency dielectric losses but does not change the frequency at which the maximum loss in each sample occurs. If the applicability of Debye's theory is accepted, this means that oxidation increases the number of polar particles per unit volume, but does not change their size. The average radius calculated from the electrical measurements is 3.4×10^{-8} cm. which is considerably smaller than the expected size of an oxidized oil molecule, and supports the statement that the whole molecule does not orient but rather the polar group moves with reference to the rest of the molecule. Thus the measurements do not give the size of the whole molecule, but do give a measure of the effective size of the portion of the molecule which is contributing to the polar moment.

3. The observed changes in capacitance factor (dielectric constant) can be predicted from the observed changes in loss factor by using Debye's theory.

4. The increase in spreading on water and the increase in high frequency losses with oxidation are found to be proportional. Since the particles which cause the spreading on water are known to be polar, this may be taken as

an argument in favor of Debye's theory as the correct explanation of the observed high frequency losses. However, when plotted, this linear relation does not pass through the origin and if the relation between losses and spreading is extrapolated back to zero spreading area, a loss factor of .02 remains to be accounted for by some other mechanism.

5. The ultramicroscope particle counts were quite erratic and showed no correlation with the rest of the measurements. The counts showed from 3×10^6 to 300×10^6 with an average value of 70×10^6 particles per cu. cm. This indicates either that the methods of sampling or counting were subject to large errors or that the suspensoids large enough to be counted were entirely unrelated to those causing changes in the other types of measurement.

6. The viscosity measurements varied slightly but no correlation was found with results of the other experiments. The observed differences were erratic and within the experimental error which was about 2%.

7. Differences of the order of 0.1% were observed in the refractive index indicating either a slight trend toward higher refractive index with greater oxidation or erratic differences of this order between samples.

The author wishes to express his indebtedness to his co-workers Dr. E. H. Winslow, M. Poggenpohl, H. I. Reynolds, and H. E. Sennett in carrying out the experiments reported in this paper.

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THE ATOMIC MASS OF SODIUM

I. The End Point of the Sodium Chloride-Silver Titration*

In recent papers¹ from this laboratory a new titration method for the accurate measurement of chemical atomic mass ratios is outlined. A unique feature of the method is the experimental elimination of all arbitrary factors in the determination of the end-point of the titration. The method is as easily applied as the usual arbitrary methods, and has the advantage of yielding far more trustworthy results.

Typical systems such as those to be obtained in the actual titration are prepared from the carefully purified products of the main analytical reaction. These systems are brought to equilibrium at a fixed temperature, and the supernatant liquids are analyzed. The equilibrium point is the correct end-point of the direct synthesis from the reactants, and may be used in deciding upon a suitable and accurate procedure for the analysis of the supernatant liquids. When, subsequently, weighed quantities of the reactants are mixed and brought to the same equilibrium point, exactly similar analyses give the data required for a correct evaluation of the ratio under consideration. The choice of the main analytical reaction, in view of the purpose of the investigation, ordinarily presupposes a complete "atom for atom" reaction in the formation and solution of the solid phase. As in all atomic mass determinations involving the formation of a precipitate in the analytical reaction, there remains a difficult question as to the purity of the precipitated compound, and adsorption effects. It is an additional advantage of the present approach to the problem that these factors may be taken into consideration.

Experimental

As an initial step in examining the general method, the conditions under which the nephelometer or potentiometer may be used in finding the correct end-point of the sodium chloride-silver titration were studied.

Reagents. The reagents used in this work were purified with extreme care, and tested to insure the absence of silver and chloride impurities. The *sodium nitrate* was a 225 gram central portion taken from 500 grams of C. P. material after six recrystallizations, with centrifugal drying. It was finally dried, fused, and weighed in platinum crucibles, without transfer. The *silver chloride* was flocculent precipitated material used in previous work, and subsequently thoroughly washed with pure water and aged over a period of ten months. This point is mentioned because of its bearing on the observed

* Contribution from the Frick Chemical Laboratory, Princeton University.

** National Research Fellow in Chemistry.

¹ J. Phys. Chem., **35**, 830, 2237, 2581 (1931).

solubility values, not because long extended soaking is considered essential to thorough washing, which may be effected quite rapidly. Other reagents were purified by the methods outlined by Scott and Johnson.¹

Typical Analytical Systems. Each of the six test systems contained 13.5 grams of thoroughly washed solid silver chloride, 7.8796 grams of sodium nitrate, and 28.46 grams of hydrogen nitrate, per 1520.7 grams of solution.

Standard Solutions. Each 1520.7 grams of standard solution contained 7.8796 grams of sodium nitrate, 28.46 grams of hydrogen nitrate, and measured equivalent amounts of silver and chloride. Correction was made for the nitrate and sodium added with the silver and chloride. Sixteen of these standards, each about 1500 grams in weight, were made during this work. Most of these solutions contained from 0.000700 to 0.001270 grams of (dissolved) silver chloride per liter, and covered this range in steps of about 0.000050 gram.

Precipitating Reagents. Solutions of silver nitrate and sodium chloride containing 1.000 mg. of silver or its equivalent of chloride per milliliter were used as precipitating reagents. Two independently prepared sets of solutions were available.

In preparing the systems described above, all measurements were made with calibrated apparatus intended to give the measurements an accuracy of 1 part in 1000 or better. Two sets of weights and balances were required. One covered the ordinary analytical range, the other was capable of weighing the large systems, contained in glass-stoppered 3-liter Pyrex Erlenmeyer flasks.

Nephelometric Tests. The typical analytical systems were either (a) frozen and melted, or (b) cooled in ice, then held at 0.2°C. during the tests made upon the supernatant liquids. The flasks were shaken once or twice only after the removal of each set of samples.

For each test two 20.00 ml. portions were taken from a filtered 50 to 100 ml. quantity of the cold supernatant liquid and allowed to come to the same temperature as two similar portions of a suitable standard solution. It was found essential to filter the cold solutions before bringing them to room temperature. Platinum Munroe crucibles and Jena sintered glass mats were suitable for the filtration, although there was evidence that silver chloride is adsorbed by the unrinsed, freshly ignited platinum mats. The effect disappeared on continued use of the crucibles. Small amounts of the solutions used in rinsing the dry pipettes, filters, and receiver were considered well spent.

In analyzing the supernatant liquids for silver, one standard and one test solution sample were treated under identical conditions with equal 2.00 ml. portions of sodium chloride solution. In analyzing for chloride, the other pair of samples was treated similarly with 2.00 ml. portions of silver nitrate solution. For each set of four solutions, contained in matched Pyrex tubes, the rates of adding the precipitating reagents and stirring were the same. It was found that the most satisfactory results were obtained when the precipitating re-

¹ Scott and Johnson: *J. Phys. Chem.*, **33**, 1978 (1929).

agents were added rapidly, with the minimum amount of stirring required to give continuous, and, finally, complete mixing, before the opalescences were well formed. Four intercomparisons of the opalescences were made about an hour after their formation. Two of these comparisons constituted a "standard-solution analysis" giving the silver and chloride content of the typical analytical system. The other two comparisons were "equal-opalescence analyses" of the standard solution and the analytical system.

Concentrations were calculated from the nephelometer scale readings in the usual manner.¹ Somewhat greater accuracy may be attained by comparing the test solution with successively converging pairs of more and less concentrated standards, regarding the relative opalescences as one considers scale readings when using a sensitive galvanometer as a null-point instrument. However, the use of this refinement may well be reserved for actual measurement of atomic mass ratios. Its effective use requires a good preliminary measurement of the ratio, and is at present limited. Calibrated photoelectric cells or thermopiles may be substituted for the eye in making the nephelometric observations, but with no particular advantage.

Results of Analyses

Results obtained in the first series of tests made with the typical analytical systems are given in Part 1 of Table I. The result of each equal-opalescence "analysis" is expressed as the average ratio of the exposed length of the cup containing excess sodium chloride to that with excess silver nitrate, at the condition of equal opalescence, as shown by the nephelometer. That is, a ratio greater than unity indicates that the samples contained excess chloride; a ratio less than unity indicates that they contained excess silver. The "actual" and observed equal-opalescence ratios should agree, if the "analysis" actually shows the relative amounts of silver and chloride in the original test solution. All except the last two columns of the table refer to the typical analytical systems, or unknowns.

A careful examination of the reagents used in the synthesis of the typical analytical systems showed that the excess of silver in Systems 1 and 2 must have come from the thoroughly washed silver chloride. The sensitivity of the tests available for detecting chloride and silver in the other reagents left no doubt upon this point. For example, when 24 grams of the sodium nitrate were dissolved in 120 ml. of water and two 20 ml. portions were tested by the equal-opalescence method, both liquids appeared quite "black" when viewed in the nephelometer, the ratio being 1.0. This test showed that the sodium nitrate contained less than six parts in four million of silver or its chloride equivalent, —the smallest amounts of these impurities which produce an unmistakably detectable deviation from the unit ratio under the conditions of the test. In a similar manner the absence of silver and chloride in the other reagents was established.

¹ J. Phys. Chem., 35, 832 (1931).

Summary of Analyses

TABLE I

Unknown Analytical Solution.	Time Cooled in Days	Standard Analyses in Milligrams Silver	Solution of Unknown. Per Liter: Chloride*	Obs.	Equal Opalescence Tests: of Unknown. Actual	Obs.	Equal Opalescence Tests: of Standard Ratio: Actual
Part 1							
1a	1	0.68	0.51	1.06	0.75	1.26	1.00
	2	0.70	0.52	1.04	0.74	1.22	1.00
1b	10	0.85	0.65	1.09	0.76	1.39	1.00
	14	0.73	0.53	1.12	0.73	1.66	1.00
	15	0.74	0.52	1.07	0.70	1.69	1.00
2a	1	0.87	0.53	0.96	0.61	1.26	1.00
	2	0.96	0.52	0.94	0.54	1.22	1.00
2b	4	0.98	0.68	1.00	0.69	1.40	1.00
	10	1.01	0.58	0.92	0.57	1.61	1.00
	14	1.03	0.56	0.89	0.54	1.35	1.00
Part 2							
3a	1	0.60	0.59	1.25	0.98	1.25	1.00
	4	0.61	0.60	1.34	0.98	1.38	1.00
	7	0.61	0.61	1.31	1.00	1.30	1.00
	8	0.59	0.59	1.29	1.00	1.27	1.00
	9	0.58	0.61	1.24	1.05	1.33	1.00
4b	9	0.63	0.62	1.58	0.98	1.55	1.00
	1	2.45	2.07	0.80	0.84	0.99	1.00
	2	0.59	0.81	1.16	1.37	1.27	1.00
	3	0.72	0.58	1.11	0.81	1.53	1.00
	4	0.63	0.63	1.33	1.00	1.33	1.00
	6	0.67	0.64	1.35	0.96	1.31	1.00
	9	0.63	0.63	1.52	1.00	1.49	1.00
	9	0.63	0.65	1.68	1.03	1.66	1.00
	10	0.61	0.59	1.36	0.97	1.48	1.00
	11	0.62	0.62	1.20	1.00	1.21	1.00
	11**	1.12	1.19	1.13	1.06	1.00	1.00
12	0.66	0.66	1.34	1.00	1.32	1.00	

* The numbers in this column are chloride concentrations, in milligrams per liter, multiplied by the factor Ag/Cl.

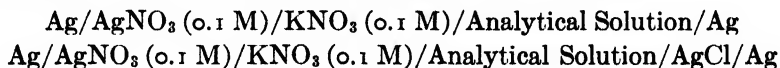
** The container was shaken 100 times and then placed in ice for one minute before removing and filtering the samples.

These experiments led to the important conclusion that precipitated silver chloride repeatedly washed with pure water separates in such a way that an excess of silver remains with the precipitate, while the washing liquid carries away more chloride than silver.¹ They also show that at least part, and possibly all, of the excess silver is removed from the precipitate by 0.3 M nitric acid (and sodium nitrate). These conclusions were further confirmed by de-

¹ See also: J. Phys. Chem., 35, 2241 (1931).

canting the supernatant liquids from the typical analytical systems and replacing them with fresh sodium nitrate-nitric acid solutions. The reagents and concentrations were the same as those used in the first syntheses. After saturating the solutions at room temperature, they were brought to 0.2°C ., whereupon the results given in Part 2 of Table I were obtained.

Analyses made with the potentiometer and the two cells:



agreed satisfactorily with the results of the nephelometric analyses. The measurements indicated that the potentiometer may be substituted for the nephelometer in these analyses without loss of accuracy. Since details of such potentiometric measurements, applied to another titration with an improved technique, are to be given elsewhere, they will be dispensed with here.

Summary

The conclusions to be drawn from the data given in Table I may be summarized: When silver chloride precipitated from nitric acid solution is repeatedly washed with pure water, the washing solution eventually contains excess chloride over silver. An excess of silver remains with the precipitate. If the non-acidified solution is decanted, and the precipitate treated with 0.3 M nitric acid (and sodium nitrate), a solution containing excess silver is obtained. If this solution is replaced by a fresh nitric acid-sodium nitrate mixture, a solution containing equivalent amounts of silver and chloride is finally obtained. The sodium nitrate has no apparent effect upon this equivalence. When the solution is frozen, melted, and cooled at 0.2°C ., the solubility of the silver chloride assumes and maintains a constant value indefinitely. This equilibrium represents a suitable reference end-point for the sodium chloride-silver titration.

The solution cooled without freezing showed irregularities doubtless due to the slow coagulation of colloidal silver chloride, but reached practically the same equilibrium point as the other solution after the fourth day. Shaking the system may increase the solubility as a temperature effect; the increase is more probably due to the formation of colloidal silver chloride. The casual, arbitrary recommendations of "occasional and frequent shaking" and "a few hours cooling," as given by investigators who have used systems of this type in atomic mass determinations, are unsound and fatal to high accuracy.

The standard solution tests, made under the conditions specified in this report, yield correct analyses of the supernatant liquids, while the equal-opalescence tests give meaningless and erroneous results. This conclusion might have been reached independently from the fact that the basis of the standard solution method of analysis is absolutely sound,—the principle that two exactly similar solutions, treated with the same reagent, will behave in the same way. The equal-opalescence method of analysis has no sound experimental or theoretical basis.

The constant error in the equal-opalescence analyses in the present case is apparently due to the unbalanced action of the dissimilar precipitating re-

agents. The effect disappears as the concentration of silver chloride in the test solution (and standard) becomes larger, i.e., when the tests are made upon solutions saturated at room temperature. In any application of the equal-opalescence method to titrations of the type under consideration, serious errors will result when the analytical systems are cooled in ice. These errors will depend upon the volume of analytical solution used, the nature and amounts of the extra compounds present, and the conditions under which the tests are made. Averaging will not remove errors of this nature from the results of faulty analyses.

The solubility values for silver chloride given in this report do not agree with those given by Hönigschmid¹ for solutions at the end-point of the sodium chloride-silver titration. It seems very probable that the disagreement is due to the fact that this investigator adjusted his analytical systems to the equal-opalescence end-point. Strictly speaking, measurements made with systems so adjusted have only a limited applicability in estimating solubility values, or, for that matter, atomic mass ratios.

The Sensitivity of the Equal-Opalescence Method

Up to the present time all estimates of the sensitivity of the equal-opalescence method of analysis have been based mainly on opinion. A general method for finding the true sensitivity of any analytical method intended for use in titrations of the present type is given by the following illustrative experiment. Two of the typical analytical systems which had been shown to contain equivalent amounts of silver and chloride were saturated at room temperature. They were then titrated away from the end-point in opposite directions, with very dilute solutions of silver nitrate and sodium chloride. The values given in the table below are the average equal-opalescence ratios found one and twelve hours after the formation of the opalescences. The tests, which were made by the method of Richards and Wells,² covered a period of about three months.

No.	Deficiency of Silver Mg./Liter	Ratio after:		No.	Excess of Silver Mg./Liter	Ratio after:	
		1 Hour	12 Hours			1 Hour	12 Hours
5	0.00	0.86	0.87	6	0.00	1.00	1.01
	0.00	0.93	1.00		0.00	0.85	1.00
	0.00	0.93	0.97		0.00	1.00	1.04
	0.10	1.04	1.03		0.08	1.01	1.02
	0.10	0.98	1.00		0.08	1.01	1.04
	0.21	0.96	1.01		0.17	1.00	1.02
	0.21	1.03	0.99		0.17	0.98	1.01
	0.33	1.22	1.23		0.27	1.02	1.04
	0.33	1.21	1.24		0.27	1.00	1.02
	0.33	1.27	1.24		0.36	0.96	1.00
					0.36	1.00	1.03
					0.45	0.74	0.79
					0.45	0.79	0.80

¹ Hönigschmid: J. Am. Chem. Soc., **53**, 3012 (1931).

² Richards and Wells: J. Am. Chem. Soc., **27**, 459 (1905)

These results removed the last apparent inconsistency between the data given in this paper and that recorded by Richards and Wells.² They explain why these investigators were consistently able to derive unit equal-opalescence ratios in "analyses" of solutions which, by their method of preparation, probably contained excess silver. In brief, the data in the above table show that the "classical" experiments of Richards and Wells do not provide an adequate experimental foundation for the use of the equal-opalescence method of analysis in the accurate determination of atomic mass ratios. There is an uncertainty of more than 0.57 milligrams of silver or its chloride equivalent *per liter* of analytical solution, in titrations made with the equal-opalescence method at room temperature. In these titrations it has been customary to use from one to five liters of solution and 0.5 to 10 gram samples of silver, in each analysis.

The failure of the equal-opalescence tests to respond to the additions of the analytical reagents may be due to the mere insensitivity of the method, or to adsorption of the added silver and chloride salts by the silver chloride precipitate. The sharp change in the nephelometric ratios eventually found on either side of the end-region argues in favor of the latter possibility. If such effects are characteristic, only the application of corrections based on analyses of the precipitated silver chloride can justify the use of the data obtained in titrations of this type, in "revising" atomic mass values.

The standard solution method of analysis is not exempt from errors due to adsorption. However, it offers the unique advantage that the absolute quantities of material entering and leaving the analytical system, and the quantities present in the liquid phase, are known at all stages of the titration. This information is essential in any attempt to analyze the precipitated compound or study adsorption effects.

General Discussion

In the case of the sodium chloride-silver titration, the standard solution method permits the excess or deficiency of silver in the analytical solutions to be determined to about 0.02 milligram for every ten grams of silver used. That is, in so far as the determination of the end-point limits the experimental accuracy, it is possible to obtain analyses correct to one part in 500,000, by the use of the procedure outlined in this paper, or by some form of *unequal-opalescence* method. Such a degree of accuracy is comparable with that which may be attained in careful weighings with a good balance, and in the other simple steps of manipulation in the analytical procedure. In general, in many other similar titrations, by the same approach, a method may be devised for bringing the analytical systems to a correct reference end-point, where the absolute amounts of excess reactant in the liquid phase may be determined by non-arbitrary tests. By working with correctly weighed amounts of the pure reactants, and applying a correction for impurities in the insoluble product, atomic mass ratios free from all sources of constant error may be obtained.

On the other hand, the application of the equal-opalescence method to the sodium chloride-silver titration would, in general, yield incorrect values for

the ratio, as the data recorded in this paper show. For example, the method of Richards and Willard,¹ if applied to this titration, might be expected to yield a low value for the sodium chloride-silver ratio. With the method of Richards and Wells,² one could obtain practically any desired or expected value, within rather wide limits, simply by making the "analyses" of the supernatant liquids under the requisite arbitrary conditions. There is evidence³ that these two equal-opalescence methods, which have been used without essential modification in many attempts to evaluate a wide variety of atomic mass ratios, fail even more seriously in other titrations.

In this connection, the fallacy of a prevalent notion concerning the high accuracy of nephelometrically determined atomic mass ratios may be pointed out. It is a peculiarity of conventional equal-opalescence atomic mass determinations that the quantities of material representing the antecedent and consequent of the ratio to be measured are weighed and combined in amounts calculated from an assumed value for the ratio. While the final adjustment to the end-point, based on tests of the supernatant analytical liquids, presumably determines the final measured value of the ratio, the initial adjustment is usually made with the expectation that the supernatant liquids will be at the end-point. With an arbitrary method of testing for the end-point, or a method insensitive to the addition of the analytical reagents to the system at the end-point, both the final value found for the ratio and its "probable error" are largely predetermined by mere opinion. The equal-opalescence method of analysis, as applied in the past, fulfills both of these requirements. The "determination of the atomic mass" by such a method is exactly analogous to the procedure of "proving" that a mass of 1.001 gram has a mass of 1.00000 gram, by showing that it gives the same point of rest, when compared by substitution weighing with a correct 1.00000 gram mass, on a balance insensitive to the difference between the masses.

It is thus quite unfair to compare the atomic mass values derived from equal-opalescence analyses with those derived by other and independent methods, using the "probable error" of the measured ratios as a criterion of their relative accuracy. The nephelometrically determined values would be given a false appearance of high accuracy and undue weight. Much excellent analytical work in this field has been overshadowed by inferior nephelometric analyses as a result of this very practice.

It may be suggested that the present tendency to reject atomic mass values from other sources in favor of nephelometrically determined values might best be justified by carrying out nephelometric analyses in a manner which would indeed make them superior to other analyses. It is with this idea in mind that the approach to the problem of accurate atomic mass measurements illustrated in the present paper has been proposed, as a general means of actually attaining the high accuracy of which the nephelometric method of analysis is capable.

Princeton, New Jersey.

¹ Richards and Willard: *J. Am. Chem. Soc.*, **32**, 32 (1910).

² Richards and Wells: *J. Am. Chem. Soc.*, **27**, 459 (1905).

³ Johnson: *J. Phys. Chem.*, **35**, 2581 (1931).

VON WEIMARN'S PRECIPITATION THEORY AND THE FORMATION OF COLLOIDAL GOLD

BY HARRY B. WEISER AND W. O. MILLIGAN

Referring to his law of corresponding states for the precipitation process von Weimarn¹ says: "Without any doubt my law of corresponding states for the crystallization process is truly a quantitative natural law." While this may be the case, one of us² has pointed out that von Weimarn's formulation has been simplified to the point where its usefulness in certain cases may be open to question. Others³ have likewise questioned the general usefulness of von Weimarn's theory. This leads von Weimarn⁴ to state: "Recently H. B. Weiser [See his book "The Colloidal Salts."] has repeated and still further extended the false view of the precipitation theory which has been credited to me. [Rept. Imp. Res. Inst. Osaka, 9, 107 (1928)]. The theory which is criticized by the authors named, did not originate with me and I yield with pleasure the honor of its discovery to one of the critics. Moreover, I have no time to clear up these misunderstandings specifically."

Von Weimarn's theory has been of such outstanding importance in pure and applied colloid science⁵ that no one can question its value. At the same time, it can do no harm to call attention to its limitations as a research tool. The recognition of such limitations in usefulness does not result from misunderstanding owing to incomplete knowledge, as von Weimarn seems to think. On the contrary, a broad comprehension of the applicability of the theory is essential to an understanding of its limitations.

In the following paragraphs the applicability and limitations of the von Weimarn theory will be considered briefly, after which its inadequacy to predict results in certain instances will be illustrated by the case of the formation of colloidal gold by reduction.

Theoretical

Von Weimarn points out that precipitation from solution takes place in two stages: the first in which the molecules in solution condense to crystalline nuclei; and the second which is concerned with the growth on the nuclei as a result of diffusion. The initial rate of precipitation W is expressed in von Weimarn's equation

$$W = K \frac{Q - L}{L} = K \frac{P}{L}$$

¹ Kolloid-Beihfte, 18, 55 (1923).

² Weiser: "The Colloidal Salts," (1928).

³ Buchner and Kalf: Rec. trav. chim., 39, 135 (1920); Bancroft: J. Phys. Chem., 24, 100 (1920); Freundlich: "Kapillarchemie," 631 (1922).

⁴ Kolloid-Z., 53, 366 (1930).

⁵ Cf. Weiser and Moreland: J. Phys. Chem., 36, 1 (1932).

where K is a constant; Q the total concentration of the substance that is to precipitate; and L its solubility. $Q - L = P$ is the absolute supersaturation and P/L is the percentage supersaturation.

The velocity of growth, V , on nuclei is given by the Nernst-Noyes equation

$$V = D/S \cdot O \cdot (Q - L)$$

where D is the diffusion coefficient; S , the thickness of the adherent film; O , the extent of surface; and Q and L have the same significance as above.

In actual practice W cannot be measured and V either cannot be measured at all or only with greatest difficulty. Accordingly von Weimarn introduced what he termed the "precipitate form coefficient" N , which is related to the mean magnitude of the single crystals in gram molecules Gm , by the expression

$$Gm \times N = \text{constant.}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression

$$N = P/L$$

which means that in the simplest case, the form of a precipitate is determined exclusively by the prevailing percentage supersaturation at the moment the precipitation starts. If this is approximately true then for the substances x , y , and z :

$$N_x = \frac{P_x}{L_x}; N_y = \frac{P_y}{L_y}; \text{ and } N_z = \frac{P_z}{L_z}.$$

Now if the mean size in gram molecules of the particles in the several precipitates is to be the same; that is,

$$\text{if, } N_x = N_y = N_z,$$

$$\text{then, } \frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}$$

This is the simplest form of von Weimarn's law of corresponding states for the precipitation process.

As would be expected the simple formulation is seldom applicable quantitatively, since in most cases there are a number of factors other than percentage supersaturation which influences the value of N and hence the mean particle size; and the magnitude of these factors is, in general, different with different substances. To take care of these several factors von Weimarn introduces a multiplier, J , into the equation for N which now becomes

$$N = J P/L.$$

But the value of J is in general not the same for different substances; hence the expression for von Weimarn's law of corresponding states becomes

$$J_x \frac{P_x}{L_x} = J_y \frac{P_y}{L_y} = J_z \frac{P_z}{L_z}$$

in which J_x , J_y and J_z are specific variable multipliers "the product of all other factors in addition to P/L which influence the crystallization process."

These factors must be expressed in abstract numbers equivalent to that for P/L .¹ This means simply that von Weimarn's law becomes quantitative and generally applicable by using variable multipliers which may include an indefinite number of unevaluated variables. Among the several factors which are lumped together in the variable multipliers are: the effect of the viscosity of the reaction medium, solvation as connected with molecular association, polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, the specific tendency to grow on nuclei, the change in solubility with particle size, etc.

The significance of the expression: $N = J P/L$ is that the mean size of the particles in a precipitate is determined by the product of the initial percentage supersaturation and of all other factors in addition to percentage supersaturation which enter into the process. In other words, the size of the precipitated particles is determined by all of the factors which enter into the precipitation process. One cannot question the truth of this statement; but it is obvious that it may not be particularly helpful in certain cases.

Fortunately, in a number of cases the von Weimarn formulation may be used to advantage in its simplest form. This is true under the following conditions: (1) if the factors influencing the precipitation process which are lumped together in von Weimarn's J are relatively unimportant as compared with the prevailing P/L value at the moment of precipitation; (2) if the factors included in J are significant but are approximately equal for the precipitation of the two or more substances under consideration. On the other hand, the von Weimarn formulation may cease to be very helpful in case the J values in the precipitation processes being compared are far from equal. This is especially true if the factors collected together in J should happen to be of greater importance than the prevailing percentage supersaturation in determining the form of the precipitate. This appears to be the case in the formation of colloidal gold by certain reduction processes to be considered in the next section.

The Formation of Colloidal Gold

In 1906 von Weimarn² formulated the rule that the mean magnitude of the individual crystals of precipitates will decrease progressively with progressively increasing concentration of reacting solutions, providing the process of direct crystallization is complete. If the form of the precipitate is determined in large measure by the prevailing percentage supersaturation, it follows from the expression

$$N = J \frac{Q - L}{L} = J \frac{P}{L}$$

that N will be larger and hence the mean size of the particles will be smaller the larger the value of Q , that is, the higher the concentration of reactants. The formation of colloidal gold by certain reduction processes is an apparent

¹ Von Weimarn: *Kolloidchem-Beihefte*, **18**, 48 (1923).

² J. Russ. Phys.-Chem. Soc., **38**, 267, 624 (1906).

contradiction to this rule. Thus Zsigmondy¹ showed in the case of the reduction by formaldehyde of HAuCl_4 made slightly alkaline with K_2CO_3 , that the greater the dilution of HAuCl_4 the higher the degree of dispersion of the particles and *vice versa*. A similar behavior was noted by Svedberg² who employed $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in alkaline solution as the reducing agent. This result would never be predicted by the von Weimarn relationship but after the fact, von Weimarn explains the apparently anomalous behavior by assuming that hydrolysis of gold salt, HAuCl_4 or KAuO_2 with the formation of $\text{Au}(\text{OH})_3$ sol which is subsequently reduced to blue $\text{Au}(\text{OH})$ sol, is the initial and therefore the significant state in determining the degree of dispersity as it is influenced by concentration of reactants. In such instances, "the principal reacting molecules are obviously the molecules of water, and it is by the ratio of their number to the number of hydrolyzing salt molecules that the velocity, as well as the degree of completeness, of the hydrolytic process, is determined."³ In other words, the greater active mass of the water and not the lower concentration of HAuCl_4 in the more dilute solutions is assumed to account for the higher dispersity in such solutions, since the higher the dilution the greater the number of nuclei formed by hydrolysis and hence the smaller the individual particles. From this point of view, it follows that if the primary particles of the $\text{Au}(\text{OH})$ ⁴ sol which is assumed to form as an intermediate product, are very small and the reducing agent insufficient, the reduction will be very slow and yet the particles will be small. On the other hand, if the originally formed particles of $\text{Au}(\text{OH})$ are relatively large the complete transformation to gold takes place slowly and the particles will be large. That is, the mean size of the primary particles in a gold sol prepared by the formaldehyde method stands in direct relation to the size of the particles of $\text{Au}(\text{OH})$ sol, the reduction of which results in the formation of colloidal gold.

The mechanism of the formation of colloidal gold which von Weimarn proposes in order to show that the process is strictly in accord with his theory is ingenious but there are certain lines of evidence which indicate that it is not correct:

In the first place Thiessen⁵ has shown that all the conditions which increase the degree of hydrolysis of HAuCl_4 solution decreases the number of particles that are formed in a given time on adding a suitable reducing agent. This is well illustrated by observation of the effect of temperature and age of HAuCl_4 solutions on the number of particles formed in a given time with hydrogen peroxide as reducing agent. In these experiments 1 cc of 0.6% $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution was added to 100 cc of water and treated with 500 cc of 5% H_2O_2 . After a definite time interval 50 cc of 0.08% $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ was added. The latter reducing agent is known to cause rapid growth on the nuclei already present and to inhibit the formation of new nuclei. A count of

¹ Zsigmondy-Alexander: "Colloids and the Ultramicroscope," 132 (1909).

² Kolloid-Z., 4, 168 (1909).

³ Von Weimarn: Chem. Review, 2, 227 (1926).

⁴ Probably hydrous Au_2O .

⁵ Kolloidchem-Beihefte, 29, 122 (1929).

the number of particles gives the number of nuclei that are present after a given time interval. The results of some observations are given in Fig. 1. The upper curve was made with freshly prepared solutions at 15° ; the middle curve with freshly prepared solutions at 21° and the lower curve with solutions previously heated to boiling and cooled suddenly to 15° . The conductivity of the fresh solution at 15° was 1.25×10^{-4} mhos and of the boiled solution at 15° was 1.37×10^{-4} mhos. The increased conductivity is indicative of an increase in hydrolysis; yet the number of particles formed with the more highly hydro-

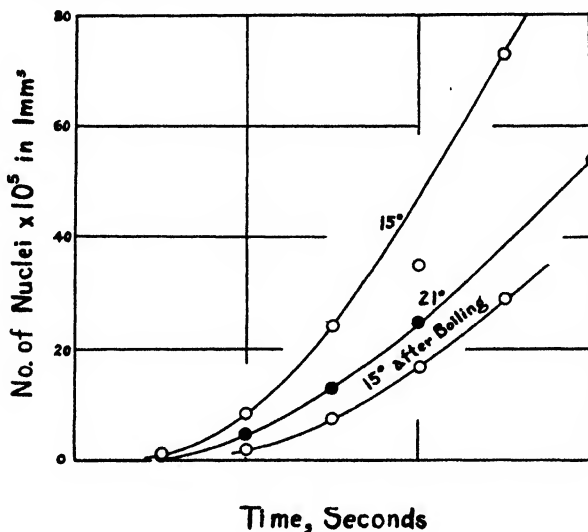


FIG. 1

Effect of treatment of HAuCl_4 Solution on the Number of Particles in a Gold Sol obtained therefrom. (Thiessen).

lyzed solution was much less and the size correspondingly greater than with the less hydrolyzed solutions. Similarly, the number of particles in a sol formed with a 10-minute old solution having a conductivity of 1.27×10^{-4} mhos was twice as great as with a 40-minute old solution with a conductivity of 1.34×10^{-4} mhos. Similar results were obtained with CO as reducing agent. These observations show that the greater the hydrolysis of the solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles. This result is diametrically opposed to what one would predict from the von Weimarn mechanism. The presence of larger particles in the more highly hydrolyzed solutions is attributed by Thiessen to a retardation of the spontaneous formation of nuclei by the hydrolysis products.

In the second place the number of particles in a gold sol is greater the higher the dilution of gold salt even when the latter undergoes little or no hydrolysis. This conclusion is reached as a result of the following experiments.

Experimental

Although a number of procedures have been described for the preparation of colloidal gold, in all but a few cases the gold was reduced from a solution of

chloraauric acid. This is prepared by dissolving metallic gold in aqua regia and evaporating to dryness. The product when dried over CaCl_2 is considered to be $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$.¹ However, some AuCl_3 will be present unless the chloraauric acid is purified in some manner. Since von Weimarn believes that the hydrolysis of the gold salt plays a significant if not a predominate part in the mechanism of the reduction of gold compounds to colloidal gold, it was thought desirable to use a gold solution in which there is little likelihood of hydrolysis. Potassium chloraurate was chosen as the most suitable gold compound for the present experiments since it is the salt of such a strong base and strong acid that it will hydrolyze but little if at all.

Preparation of KAuCl_4 . Pure sheet gold was dissolved in aqua regia, the excess acids removed by boiling, and the resulting chloraauric acid extracted from the aqueous solution with ethyl acetate.² The chloraauric acid was crystallized from the ethyl acetate, dissolved in distilled water, and allowed to react with the calculated quantity of recrystallized potassium chloride. The resulting KAuCl_4 was crystallized from aqueous solution by slow evaporation in a vacuum desiccator over H_2SO_4 . Finally the best crystals were separated mechanically, washed with anhydrous ether,³ and the excess ether removed in a vacuum desiccator. The gold content of the crystals was obtained without attempting to dry them to any definite composition. A 0.01 molar stock solution of KAuCl_4 was made up from which other solutions were prepared by dilution.

The Distilled Water. The purity of the distilled water used is an important factor in the preparation of colloidal gold. Much has been written by Zsigmondy and others⁴ concerning the necessary purity of the distilled water. In view of the fact that a solution of electrolytes is reduced and electrolytes are formed as products, it is apparent that slight traces of electrolyte impurities in the water employed will have little or no effect. Organic material, dust particles, etc., which can serve as nuclei are the undesirable variable impurities that may be in the distilled water. Accordingly water of minimum conductivity is not necessarily the best to use. In the present investigation water prepared by a single distillation of ordinary laboratory grade distilled water in a copper still with a block tin condenser gave the same results as the same water distilled twice more from KMnO_4 and H_2SO_4 respectively, in a pyrex still with a block tin condenser. However, care was used to let the distilled water stand for several days in an aged bottle, and to syphon off the water, taking the precaution not to disturb the lower layer, into which the undesirable dust particles had settled.⁵ This distilled water was used in the experiments about to be described.

Size of Au Particles in Sols formed by Reduction of KAuCl_4 with H_2O_2 . Amounts of solution as indicated in Table I were mixed together in the follow-

¹ Lengfeld: Am. Chem. J., 26, 328 (1901).

² Lenher and Kao: J. Phys. Chem., 30, 126 (1926).

³ Mylius and Hüttner: Ber., 44, 1315 (1911).

⁴ Zsigmondy-Thiessen: "Das kolloide Gold" (1926).

⁵ Zsigmondy-Alexander: "Colloids and the Ultramicroscope "

ing manner: To the water in a 250 cc pyrex flask was added first the KAuCl_4 solution and then 0.2 cc of 30% H_2O_2 . The latter was allowed to flow in from a pipette while the contents of the flask were shaken with a rotary motion. The reduction was carried out at room temperature. A tint of color appeared in about 30 seconds, and the reaction was complete as evidenced by no further change in color in two or three minutes. Tests disclosed the absence of un-reduced gold in the supernatant solution after coagulation of the sol. A clear, red, colloidal gold solution was obtained in each case. The number of particles

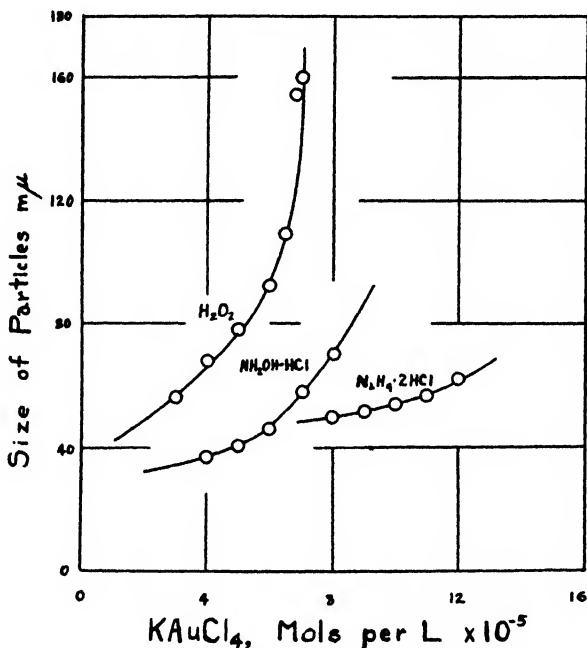


FIG. 2

Effect of Concentration of Gold Salt Solution on the Size of Particles of Colloidal Gold obtained by reduction with H_2O_2 , $\text{NH}_2\text{OH} \cdot \text{HCl}$ and $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

TABLE I

Size of Au Particles formed by Reduction of KAuCl_4 with H_2O_2

Solutions mixed			Resulting concentration of KAuCl_4 Molarity $\times 10^{-5}$	Mean linear dimension of Au particles m μ
KAuCl_4 0.001 M cc	H_2O cc	H_2O_2 30% cc		
7	92.8	0.2	7	160
6.75	93.05	0.2	6.75	155
6.5	93.3	0.2	6.5	109
6	93.8	0.2	6	92
5	94.8	0.2	5	78
4	95.8	0.2	4	68
3	96.8	0.2	3	56

in a definite volume of sol was counted in the usual way by means of the Zeiss Slit Ultramicroscope. From the data so obtained the particle size was calculated assuming the particles to be cubic. The results are given in Table I and shown graphically in Fig. 2.

Size of Au Particles in Sols formed by Reduction of KAuCl_4 with $\text{NH}_2\text{OH}\cdot\text{HCl}$. In the reduction with H_2O_2 , a constant amount of reducing agent was used. This was permissible since the excess H_2O_2 has little or no effect on the size of the particle.¹ Since this is not the case with many reducing agents, in the subsequent experiments a constant mole ratio of the KAuCl_4 and the reducing agent was maintained. Solutions A and B prepared as indicated in Table II were mixed together. In every case a clear, red colloidal gold solution resulted. The particle size in each was determined with the results recorded in the table and shown graphically in Fig. 2.

TABLE II

Size of Au Particles formed by Reduction of KAuCl_4 with $\text{NH}_2\text{OH}\cdot\text{HCl}$

Solutions mixed				Resulting concentration of KAuCl_4 Molarity $\times 10^{-6}$	Mean linear dimension of Au particles $m\mu$
A		B			
KAuCl_4 0.001 M cc	H_2O cc	$\text{NH}_2\text{OH}\cdot\text{HCl}$ 0.00375 M cc	H_2O cc		
8	42	8	42	8	70
7	43	7	43	7	58
6	44	6	44	6	46
5	45	5	45	5	41
4	46	4	46	4	37

Size of Au Particles in Sols formed by Reduction of KAuCl_4 with $\text{N}_2\text{H}_4\cdot 2\text{HCl}$. The reducing agent was added to the several concentrations of KAuCl_4 solutions as given in Table III. The size of the gold particles in each of the clear red sols was determined. The results are given in the table and shown graphically in Fig. 2.

TABLE III

Size of Au Particles formed by Reduction of KAuCl_4 with $\text{N}_2\text{H}_4\cdot 2\text{HCl}$

Solutions mixed			Resulting concentrations of KAuCl_4 Molarity $\times 10^{-6}$	Mean linear dimensions of Au particles $m\mu$
KAuCl_4 0.001 M cc	H_2O cc	$\text{N}_2\text{H}_4\cdot 2\text{HCl}$ 0.001 M cc		
12	76	12	12	62
11	78	11	11	57
10	80	10	10	54
9	82	9	9	52
8	84	8	8	50

¹ Westgren: Z. anorg. Chem., 93, 154 (1915).

Conclusions

The particles of colloidal gold formed by reduction processes are larger the higher the concentration of the gold salt reduced. This is not in accord with von Weimarn's theory which states that, provided the process of crystallization is complete, the mean size of the individual crystals is smaller the higher the concentration of the reactants. Von Weimarn explains this anomalous behavior by postulating that hydrolysis of the gold salt with the formation of $\text{Au}(\text{OH})_3$ which is subsequently reduced to $\text{Au}(\text{OH})$ and finally to Au is the initial and therefore the important step in determining the degree of dispersity as it is influenced by the concentration of reactants. From this point of view the greater hydrolysis at lower concentrations accounts for the greater number of nuclei and hence the smaller size of the particles in low dilution. Against this point of view are: (1) Thiessen's observations that the greater the hydrolysis of the gold solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles; and (2) the observations herein recorded which show that in the absence of appreciable hydrolysis of gold salt the gold particles are smaller the more dilute the solution.

It is apparent from these considerations that the percentage supersaturation at the beginning of precipitation is not the only factor and may not be the most important one in determining the primary particle size in the formation of colloidal gold. In the absence of added nuclei, the size of the primary gold particles in a sol will be determined, for a given concentration of reactants by the velocity with which nuclei form spontaneously and the velocity with which the particles grow on the spontaneously formed nuclei. Now it is to be expected from the Nernst-Noyes formulation that the velocity of growth on added nuclei will be greater the greater the absolute supersaturation of the solution with respect to gold; in other words, the greater the initial concentration of gold salt. The same thing will apply to the rate of growth on nuclei formed spontaneously. In general to obtain very highly dispersed particles, the velocity of formation of nuclei must be relatively rapid and the growth on the effective nuclei must be relatively slow. Since gold is extremely insoluble, the percentage supersaturation of the metal is relatively high at all concentrations of the gold salt under consideration. Under these conditions the rate of formation of nuclei is not directly proportional to the percentage supersaturation but is relatively more rapid at the higher dilutions. Moreover, at the higher dilutions the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is exhausted. For both of these reasons the size of the primary particles is smaller in the sols formed from the more dilute solutions of gold salt.

Von Weimarn may contend that larger particles formed in the more concentrated solutions are aggregates rather than primary particles. There is no evidence to support this view under the experimental conditions herein described. All the sols were perfectly clear and the ultramicroscopic examination showed no indication of aggregate formation. Moreover, it is well known that particles grow by direct precipitation of gold on gold nuclei added to the reduction mixture and there is no reason to believe that the process is any differ-

ent in the presence of spontaneously formed nuclei. In this connection, if one insists that $\text{Au}(\text{OH})_3$ and $\text{Au}(\text{OH})$ are precipitated as intermediate products in the reduction process, then the growth on gold nuclei must result from initial precipitation of $\text{Au}(\text{OH})_3$ on such particles followed by reduction to $\text{Au}(\text{OH})$ and subsequently to gold. While this could be true to a certain extent, it seems to be altogether unnecessary to assume such a mechanism since it is probably not in general accord with the facts.

Summary

The following is a brief summary of the results of this article.

1. Von Weimarn's formulation of the precipitate form coefficient and the law of corresponding states for the precipitation process have been considered from the standpoint of their applicability and limitation as a research tool.

2. The particles of colloidal gold formed by reduction processes are in general larger the higher the concentration of the gold salt reduced. This would not be predicted from the von Weimarn theory which states that, provided the process of direct crystallization is complete, the mean size of the individual crystals is smaller the higher the concentration of reactants (the higher the percentage supersaturation at the moment precipitation begins).

3. Von Weimarn explains the apparently anomalous behavior noted in (2) by postulating that hydrolysis of gold salt with the formation of $\text{Au}(\text{OH})_3$, which is subsequently reduced to $\text{Au}(\text{OH})$ and finally to Au , is the initial and therefore, the important step in determining the degree of dispersity as it is influenced by the concentration of reactants.

4. Against von Weimarn's general point of view are the observations: (a) the greater the hydrolysis of gold solution of a given concentration, prior to the addition of reducing agent, the fewer the number and hence the larger particles of gold (Thiessen); (b) the observations recorded in this paper which show that in the absence of hydrolysis of gold salt, the gold particles are smaller the lower the concentration of the salt reduced. This was found to be true for the reduction of solutions of KAuCl_4 with H_2O_2 , $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{N}_2\text{H}_4\cdot 2\text{HCl}$.

5. Because of the very low solubility of gold in water, the percentage supersaturation of the metal is relatively high at all concentrations of gold salt reduced. Under these conditions the rate of formation of nuclei is not directly proportional to the percentage supersaturation but is relatively more rapid at the higher dilutions. Moreover at the higher dilutions the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is exhausted. For both of these reasons the size of the primary particles is smaller in the sols formed from the more dilute solutions of gold salt.

THE THERMAL DECOMPOSITION OF DIMETHYLAMINE

BY H. AUSTIN TAYLOR

Previous kinetic studies of the decompositions of ethylamine,¹ of propylamine² and of isopropylamine³ have shown that although the reactions are complex it is reasonably certain that the initial process is homogeneous and unimolecular in each case. The observed decrease in the rates of decomposition for propylamine and isopropylamine, with decreasing pressure led to the conclusion that activation of a single vibrational bond alone was involved. Such an apparent simplicity is to be contrasted with the very complex mechanisms involved in the activation process of other unimolecular reactions. In an effort to see what effects a secondary amine would have on such results the present investigation was carried out and although appearing on the surface to be very similar, its extreme complexities suggest that the simplicity of mechanism of activation is probably fortuitous due to a mutual compensation of several reactions. Further work on the amines is still in progress but it seems advisable that a report of the type of complications involved should be given since a similar condition may possibly account for certain peculiarities in other cases.

The apparatus and procedure were identical with those already published. The results at pressures below 15 mms. were obtained by the use of a sloping manometer whereby the pressure change was multiplied by a factor of 8.26. The dimethylamine was redistilled from an Eastman sample and showed a small trace of a primary and tertiary amine. The decomposition was studied over the temperature range 480-510°C. at pressures from 3.75 to 600 mms. The pressure increase during reaction averaged 120 percent although a slight drift with pressure was noticeable, the increase being greater at lower pressures. No effect of temperature on this value could be observed.

The increases in pressure plotted against time give typical unimolecular rate curves showing, however, a very slow but continued pressure increase towards the end of the reaction. It was necessary therefore to follow a reaction which for example had a quarter life of 3 minutes, about 15 hours to obtain a reliable end-point.

In Table I are given the quarter lives for the various temperatures and pressures studied, calculated as the time taken for the pressure to increase by one-quarter of the total change.

The natural conclusion from such a constancy of the quarter lives at the higher pressures is that the reaction is unimolecular. At lower pressures the order of reaction would appear to be between one and two.

¹ J. Phys. Chem., **34**, 2761 (1930).

² J. Phys. Chem., **35**, 2658 (1931).

³ J. Phys. Chem., **36**, 670 (1932).

TABLE I

Initial Pressure in mms.	t_{25} mins.	Initial Pressure in mms.	t_{25} mins.
Temperature 480°C.			
88	9.9	279	5.8
133	8.8	333	5.3
181	7.8	597	4.6
Temperature 490°C.			
81	6.5	229	4.6
120	5.6	303	3.8
176	5.2	555	3.0
Temperature 500°C.			
5.8	10.0	161	2.8
15	8.0	198	3.0
53	5.4	251	2.4
105	3.5	315	2.2
116	3.1	547	2.1
Temperature 510°C.			
3.75	7.8	297	1.5
14.8	4.9	404	1.4
44	3.6	409	1.5
90	2.6	421	1.5
160	2.2	486	1.4
173	2.2	522	1.5
225	2.0	524	1.3
252	1.8	622	1.45

Since a change in end-point had been observed with change in initial pressure it seemed possible that the reaction might be in part at least heterogeneous. On increasing the surface of the pyrex reaction vessel by the addition of measured lengths of pyrex tubing whereby the surface to volume ratio was increased 3.4 times, the quarter lines given in Table II were obtained.

TABLE II

Increased Surface ($S/V = 3.4$) Temperature 510°C.

Initial Pressure	t_{25}
4	8.0
41	4.0
161	2.2

These values, it will be seen, are in substantial agreement with those previously quoted showing the absence of any marked heterogeneity.

Assuming then the reaction to be homogeneous and unimolecular it will be seen that at 510°C . the velocity constant appears to fall off below about 300 mms. It is of interest to see the effects of various added gases. The effect of the reaction products was first investigated. The decomposition of 120 mms. of dimethylamine was allowed to go to completion. A further charge of amine was then added and the rate followed in the usual manner. Two such runs were made in the pressure region where the reaction rate had fallen off namely at 94 and 44 mms. each with the products from 120 mms. of the amine present. The quarter life was 2.0 minutes in each case as compared with 2.6 and 3.6 minutes, respectively, obtained in the absence of products. It appears, therefore that the products are capable of maintaining the rate somewhat in the lower pressure range. A similar effect was observed with hydrogen, ethane and ammonia. With 200 mms. of hydrogen the quarter lives of 39 and 161 mms. of amine were 2.4 and 1.6 minutes, respectively, compared with 3.9 and 2.2 minutes without hydrogen. A similar amount of ethane gave times of 2.8 and 1.6 minutes for 47 and 162 mms. of amine whilst 200 mms. of ammonia gave for 46 and 164 mms. of amine quarter lives of 2.8 and 1.6 minutes. In all the reactions involving either the products, hydrogen or ethane the end-point of the decomposition was the same as in the absence of added gases. With ammonia, however, the total pressure increase rose from 125 to 135 percent of the initial amine pressure which might suggest some actual chemical interaction although even this extent of change is not as great as the 150 percent observed with 4 mms. initial pressure of amine alone. With ethylene as added gas more definite evidence of reaction was obtained. Even making due allowance for the pressure decrease due to polymerisation of the ethylene, data for which were obtained from a blank run with ethylene alone, the observed pressure increase due to the amine was only 80 percent of the initial pressure. The general course of the reaction too was quite changed notably with respect to the end-point which was reached very sharply after only 40 minutes in comparison with the several hours necessary with amine alone. A comparison of the rate of reaction in presence of ethylene with that in its absence is thus impossible.

One definitely inert gas was tried namely nitrogen and found to be without effect at any stage of the reaction. When 200 mms. of nitrogen were added to 161 and 485 mms. of amine quarter lives of 2.2 and 1.5 minutes were obtained in complete agreement with the values obtained for the amine alone.

Such a behavior by a reaction would appear to be best explained on the assumption that the reaction is unimolecular. The constancy of rate at higher pressures, its falling value at lower pressures, the absence of effect of truly inert gases at any pressure, the maintenance of the high pressure rate in the low pressure region by certain complex molecules with absence of effect by the same molecules in the high pressure range are all usually accepted as unequivocal evidence of unimolecularity in a reaction.

The reaction rates obtained may thus be compared with others similarly obtained. The energy of activation obtained by plotting the logarithms of the limiting quarter lives at higher pressures against the reciprocals of the

corresponding absolute temperatures and taking the slope of the straight line so given is found to be 44,300 calories. The value is identical within the limits of error with that obtained for ethylamine and for propylamine. With this value one can calculate that a reaction would occur with a velocity constant of $0.00158 \text{ sec.}^{-1}$ corresponding to a quarter life of 3.0 minutes at 489°C . At this temperature the value of E/RT would be 29.3 as compared with 28.2 obtained for ethylamine and 28.9 for propylamine. Taking the falling off as occurring around 400 mms. at this temperature, the number of molecules entering into collision under these conditions is 2.7×10^{28} per cubic centimeter per second using a molecular diameter of 7×10^{-8} cms. The number of molecules reacting similarly is 4×10^{15} giving a ratio of 1.5×10^{-13} . The value of $e^{-E/RT}$ is 1.8×10^{-13} an agreement which would only be possible with a molecular model involving one or two effective degrees of freedom, a condition similarly found for the other amines studied.

Despite the apparent consistency between all the amines so far studied there is certain evidence that the results may be misleading, certainly in this case with dimethylamine and possibly in the previous ones also. It seems hardly conceivable that an extremely complex reaction could yield reaction rates which on the surface appear to agree so well with accepted theories of unimolecular reactions. The percentage pressure increase during the reaction could well be accounted for on the basis of a single molecule yielding two molecules on initial decomposition followed by a small further decomposition of the products. Such a split in the case of dimethylamine might be presumed to yield ammonia and ethylene. An analysis of the products of decomposition after one of the above runs showed no ammonia present and no unsaturated hydrocarbon. The quantity of material available for analysis in any single experiment as actually carried out in a static manner being small, a definite weight of the dimethylamine was scaled in an evacuated glass bulb and placed in the furnace for a sufficient time for reaction to be complete. The bulb was then cooled and the contents analysed. The appearance of the bulb before opening was surprising, for despite the fact that the vessel used in the static experiments was perfectly clean after several hundred runs and that only a small amount of a dark brown liquid had collected in the capillaries just outside the furnace, the bulb was black and quite opaque to light. It should be noticed, however, that the actual concentration in the latter case was very considerably greater than in any one of the static experiments. The bulb was opened over water in such a way that the insoluble gases could be collected and measured. For about an hour after the bulb had been opened a contraction in the volume of the system was observed pointing to a slow solution of some constituent. Analysis of the fixed gas showed it to contain 65 percent methane, 30 percent ethane and 5 percent hydrogen, no free nitrogen being present. An acid titration of the aqueous solution yielded only 0.4 of the nitrogen initially present in the amine taken. The bulb still carrying its black coating was next examined. The odor was entirely different from that of an amine, being almost putrid. The addition of hydrochloric acid, however, caused most of the black coating to dissolve as a dark brown solution carrying

a small amount of a black solid in suspension, presumably carbon. The amount of this latter acid addition made up almost completely for the nitrogen content of the amine taken. By subtracting the amount of hydrogen and carbon found from the initial amine taken an empirical formula for the residue of CH_6N_3 was found. Though probably not guanidin, as this might suggest, the final product must be some complex nitrogenous material of that type.

In an effort to isolate any intermediate substances that might be formed during the reaction several dynamic runs were made. The dimethylamine was allowed to evaporate under its own vapor pressure at room temperature through a small capillary into a furnace kept at 500°C . The products obtained consisted of a colorless liquid with strong ammoniacal odor but penetrating after-effect suggestive of a hydrazine. It boiled over a range from about 70 to 110°C ., reduced silver oxide in the cold and decomposed at 500°C . in a static run with a pressure increase at a rate almost ten times as great as that of the dimethylamine. The liquid contained a small amount of a white solid, soluble in water but insoluble in ether, which sublimed without melting at about 250°C . and gave a dull orange precipitate with iodine in potassium iodide. Analysis of the fixed gases showed 60 percent of hydrogen and 40 percent of ethane. The aqueous solution over which the gases were collected showed unchanged secondary amine and a trace of ammonia shown by the insoluble sodium ammonium cobaltinitrite. It seems probable, therefore, that the products contain chiefly methyl hydrazines, the solid being probably hexamethylene tetramine.

On raising the temperature of the furnace to 600°C ., using the same rate of flow of amine as previously, the liquid which collected was no longer colorless but decidedly brown, its complexity being shown by its boiling point range from about 40 to 130°C ., there being some constituent present decidedly more volatile than in the liquid previously obtained at the lower temperature. This more volatile constituent decomposed at 500°C . in a static experiment with a pressure decrease at a rate which was about five times as rapid as the rate of pressure increase of the original amine. Furthermore, the brown liquid maintained at 100°C . gradually developed larger quantities of the more volatile constituent decomposing with a pressure decrease. This pressure decrease was undoubtedly due to a polymerisation to a high boiling product which subsequently condensed in the capillaries outside the furnace, as considerable difficulty was experienced in evacuating the system after these experiments.

The decomposition of dimethylamine under the conditions of the static experiments therefore must be extremely complex and the observed rate of pressure increase, a composite of at least two rates in opposing directions. It would appear that methyl hydrazines are the chief constituent in the lower temperature dynamic runs and presumably therefore are easily formed from dimethylamine. Their formation should occur as a bimolecular reaction. If the subsequent decomposition of the hydrazine was unimolecular one would expect an induction period in the net rate unless the primary bimolecular reaction was much more rapid than the unimolecular. In this latter event a

lowering of temperature might possibly permit a separation of the two. No such change could actually be found. This of course may simply mean that the energies of activation of the bimolecular and unimolecular rates are approximately the same.¹ In any event the very rapid rate of decomposition of the hydrazines is being offset by the reaction with the pressure decrease.

It seems almost phenomenal that such a complex reaction should yield what are apparently simple data and one naturally wonders whether it is possible to reproduce for example pressure-rate curves such as are being accepted as typical of true unimolecular reactions by a counterbalancing of effects in two or more reactions proceeding simultaneously. It may be shown in certain cases that a bimolecular polymerization proceeding simultaneously with a unimolecular decomposition may give a logarithmic relation between initial pressure and half-life as calculated from the observed pressure change. Should the form of this logarithmic relation be such as to bring the asymptotic portion of the curve within easily measurable pressure ranges an apparently constant half-life with changing initial pressure would be observed and might be mistaken for a true unimolecular reaction whose rate decreased at lower initial concentrations. Whether such is the explanation of the case here studied remains for further work to prove.

One rather significant feature of the results obtained, lies in the rapidly falling values calculated for the velocity constants in any run, despite the fact as shown that the products of the reaction tend to maintain the high pressure

TABLE III

Temperature 510°C.		Initial pressure 486 mms.	
Time	ΔP	k_1	$k_2 \times 10^3$
1	125	.217	.379
2	205	.193	.368
3	269	.182	.378
4	314	.169	.376
5	351	.159	.380
7	407	.144	.390
9	441	.130	.390
11	469	.120	.390
13	489	.111	.389
15	503	.103	.382
20	527	.087	.364
25	543	.076	.350
30	553	.067	.331
40	567	.054	.303
50	578	.047	.291
60	587	.042	.288

¹ A case in point is actually found in the decomposition of ethyl mercaptan to be published shortly.

rate. Table III gives a typical example of the calculated velocity constants, k_1 being the unimolecular constants, k_2 the bimolecular constants. It will be noted that the values of k_2 are much better than k_1 although from the quarter lives the reaction cannot possibly be bimolecular.

In conclusion one further point may be raised. The accompanying diagram shows the curves obtained by plotting the quarter lives against initial

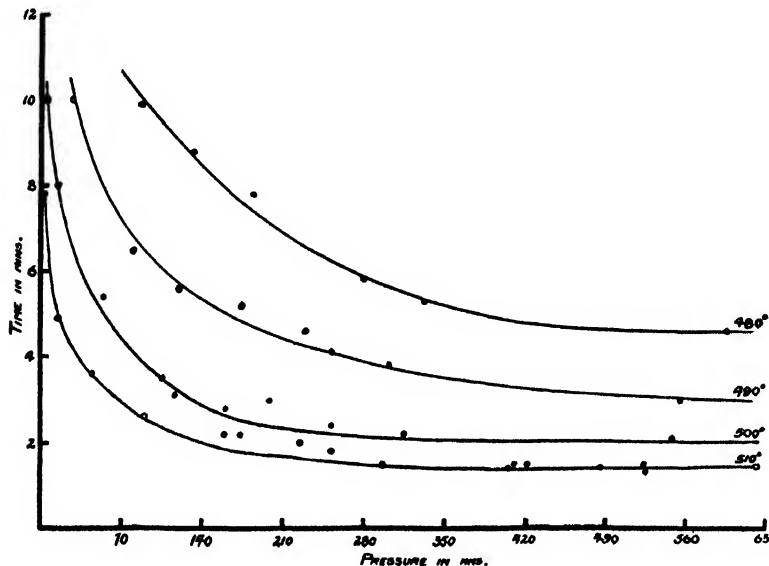


FIG. 1

pressures at the four temperatures studied. The forms of the curves might well be those of a unimolecular reaction were it not for the fact that the reaction rate appears to decrease at a higher pressure the lower the temperature. Such a variation is contrary to the usual expectation for a unimolecular reaction. A plot of the quarter life against the reciprocal of the initial pressure gives at each temperature curves showing such a marked curvature that an extrapolation to determine the limiting quarter life at high pressures is doubtful but would indicate that the limiting value has not been reached at 600 mms. at the lowest temperature studied.

Summary

The rate of pressure increase in the decomposition of dimethylamine over a temperature range from 480 to 510°C. appears to indicate a homogeneous unimolecular reaction with an energy of activation of 44,300 calories. Dynamic investigations show the reaction to be so extremely complex as to cast doubt on the above interpretation. Further work is in progress.

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THE MELTING POINT OF BENZENE

BY ALAN W. C. MENZIES AND D. A. LACOSS

A few months ago, Irvine Masson reported¹ that he had found the melting point of benzene, measured by duly standardized thermometers, at 5.58° . As to the benzene used, he considered that "the impurity, if any, was . . . extremely small." He therefore stated that it appeared that "the melting point of benzene suggested by T. W. Richards² as 5.493° is about 0.1° too low and should not be taken as a fixed point in precise thermometry."

It may be pointed out that, while Richards' benzene was saturated with "air," Masson's was presumably saturated with hydrogen, and that one would, therefore, have anticipated, on account of the lower solubility of hydrogen in benzene,³ that Masson's freezing point would be higher. But the difference anticipated from this cause would, we compute, reach only 0.017° , and is thus insufficient to account for the discrepancy.

We have recently reported⁴ that a number of the physical properties of liquid benzene, as recorded in the literature, exhibit an alteration of rate of change with temperature at a temperature near 40° . Having established this unexpected abnormality for benzene, which seems to have escaped notice these many years, we were prepared for any other abnormality of benzene that might present itself.

Masson froze his specimen of benzene rather slowly, so that it took eleven hours to freeze out 210 gm. In the work of Richards, the rate of freezing was doubtless much faster.

In these circumstances it seemed worth while to examine the freezing point of the same sample of benzene under conditions which would permit of varying widely the rate of formation of the solid phase.

In our other work with benzene, we have used the highest qualities of coal tar benzene obtainable commercially, and, after taking precautions to remove such impurities as thiophene, carbon bisulphide and water, have obtained freezing points in air at atmospheric pressure in agreement with Richards. The same thing is true of samples which we have prepared from benzoic acid of the highest purity. For the present purpose, we employed a sample of this kind, purified by fractional distillation and fractional freezing and dried by refluxing over three separate quantities of metallic sodium, the last of which remained bright. The refractive index for the D lines of sodium was 1.5014 at 20° .

Using a technique which we employ in experiments on intensive desiccation, we sealed up about 20 grams of liquid benzene along with nitrogen at

¹ *Nature*, **128**, 726 (1931).

² Richards, Carver and Schumb: *J. Am. Chem. Soc.*, **41**, 2019 (1919).

³ J. Horiuti: *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **17**, 125 (1931).

⁴ Menzies and Lacoss: *Proc. Nat. Acad. Sci.*, **18**, 144 (1932).

atmospheric pressure in the space, of annular cross-section, between two Pyrex glass tubes of about 10 and 20 mm. bore, respectively, one of which lay coaxially within the other. Both of these tubes, of lengths about 8 and 12 cm., respectively, were closed at one end; at the other end, the outer was closed by a ring seal to the inner tube, which was prolonged into a graduated capillary, bent at a convenient angle. The inner tube and its capillary extension were charged, by the boiling-out process used in filling thermometers, with ethyl ether in such a way as to form a differential thermometer sensitive to 0.005° . The bulb of this thermometer was thus situated in the central portion of an all-glass chamber which was two-thirds filled with the benzene. The benzene chamber was furnished with an air-jacket, and the whole could be immersed and rocked mechanically in a thermostat. Crystallization could be induced in the benzene when even only slightly under-cooled by touching a portion of the glass enclosing the liquid momentarily with carbon dioxide snow. The rate of growth of the benzene crystals could be controlled with great ease by regulating the temperature of the thermostat. Slower cooling gave much larger crystals, in spite of the rocking motion of the apparatus.

In one experiment about 14 grams of crystals were grown uniformly over a period of six hours, which is slower than Masson's rate of growth. In another experiment the rate of growth was twenty times as fast, which is presumably faster than that of Richards' experiments. In all cases the equilibrium temperature for solid and liquid benzene was remarkably steady, whether the environment were hotter or colder, and we found no difference in temperature dependent on rate of freezing exceeding 0.01° .

Although we were interested primarily in relative rather than absolute values, we redetermined the zero points of and made comparison with two thermometers furnished with Reichsanstalt certificates of corrections to $\pm 0.02^{\circ}$ at 0° and 10° ; and, further, made comparison, through the courtesy of a colleague, at two points distant not over 1° from the benzene freezing point with a platinum resistance thermometer of which we believe the readings are good to hundredths of a degree. These agreed in yielding a freezing point for our nitrogen-saturated benzene under atmospheric pressure of $5.49 \pm 0.02^{\circ}$, a value in concordance with that reported by Richards. The small temperature difference which would be attributable to the molecular solubility difference of nitrogen as opposed to air is well within our error of experiment.

Summary

- 1). Although liquid benzene has been shown to exhibit an anomalous behavior near 40° , this liquid, at constant pressure, solidifies at a constant temperature, independent of the rate of freezing.
- 2). Contrary to the recent criticisms of Masson, we find no reason to doubt the value for the benzene freezing point reported by Richards, Carver and Schumb.

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NINTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS*

BY J. N. PEARCE

The yearly contribution of research in the field of heterogeneous catalysis is increasing with leaps and bounds. It overlaps and permeates other fields and, in turn, is overlapped and permeated by these to such an extent that it is difficult sometimes to differentiate between that which should be included in such a report and that which should be excluded. To read critically each of the numerous papers appearing yearly in this field is a considerable task. Many of these deal with new applications of old processes or new syntheses with familiar catalysts,—all of which are valuable indeed. There are those which contribute new ideas, new viewpoints and new theories. These theories may in time prove to be unsound and may be relegated finally to the museum of forlorn attempts to arrive at an understanding of the processes in heterogeneous catalysis. Whether right or wrong, they are of value in that they stimulate research, the results of which may help us, or those who follow, someday, sometime to know the truth.

While many accounts of catalytic reaction are recorded, an attempt has been made to include, when possible, those researches which deal with the theory and mechanism of adsorption. It is possible that some important work may have been passed over too lightly, or omitted altogether. Since the same opinions are not shared by all, apologies are extended for both sins of omission and commission.

Surface Considerations

Ogawa¹ was the first to observe that only those charcoals will adsorb alkali from solution which have been activated at moderate temperatures. This adsorptive property is for the most part destroyed by activation at high temperatures. Dubinin² has found that charcoals which are activated at 550° are capable of adsorbing alkalies; they lose this property when heated to 1100° in a vacuum; exposing the glowed charcoal to air for a short time at moderate temperature is sufficient to restore its activity and its adsorptive capacity for alkalies.

Schilov and Tschmutov³ have shown that in the adsorption of electrolyte by charcoal, which has been in contact with air, carbon dioxide is formed as a result of hydrolytic cleavage in the solution. Exposure of gas-free charcoal to

* Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by J. N. Pearce with the assistance of the other members of the Committee: Messrs. Homer Adkins, E. Frankland Armstrong, Oliver W. Brown, Robert E. Burk, J. C. W. Fraser, E. Emmet Reid, Guy B. Taylor, H. S. Taylor, and W. D. Bancroft, Chairman.

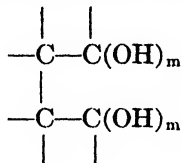
¹ Ogawa: *Biochem. Z.*, **161**, 275 (1925); **172**, 249 (1926).

² Dubinin: *Z. physik. Chem.*, **140**, 81 (1929).

³ Schilov and Tschmutov: *Z. physik. Chem.*, **133**, 188 (1928).

air for a short time is sufficient for the formation of detectable amounts of carbon dioxide in the charcoal.

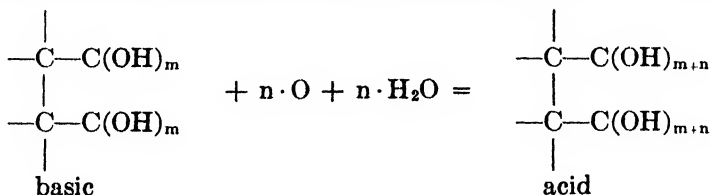
It was these relations that led Schilov to the view that the adsorption of alkalis is accomplished through the carbon dioxide formed by the oxidation of the charcoal. Recent experiments¹ show that with increase in pressure from 10^{-6} to 2 mm. there is formed on the surface a complete film of active oxide which cannot be removed by evacuation or heating. Since the magnitude of the adsorption depends only on the amount of surface oxide, the quantity of hydrochloric acid adsorbed by the charcoal is constant and independent of the oxygen pressure. The adsorption then increases rapidly to about a four-fold value and again remains practically constant with further increase in oxygen pressure. This primary oxide reacts with the water forming a "carbon hydroxide":



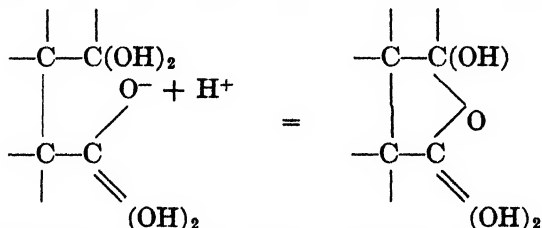
They assume that the adsorption of the hydrochloric acid at low oxygen pressure is a reaction between this hydroxide and the hydrochloric acid.

The steep rise in the curve corresponds to a further oxidation and the subsequent approximate constant portion points to a saturation of the carbon surface. The surface becomes electrically charged through the formation of oxide and hydroxide and can take up definite amounts of molecular oxygen. This carbon hydroxide can form hydroxyl ions: hence the active surface can adsorb acids, but it cannot adsorb alkalis.

The secondary oxide, unlike the primary, possesses an acid nature, and with water it forms polyhydroxide compounds analogous to the orthoacids:

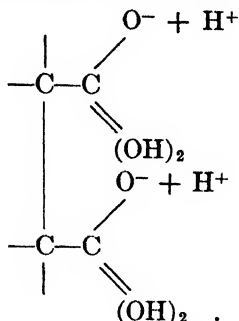


As to the adsorption of alkalis there are three possibilities depending upon the three possible different states of the charcoal surface. The first corresponds to the formation of an inner salt, or anhydrous oxide which is stable toward alkalis:



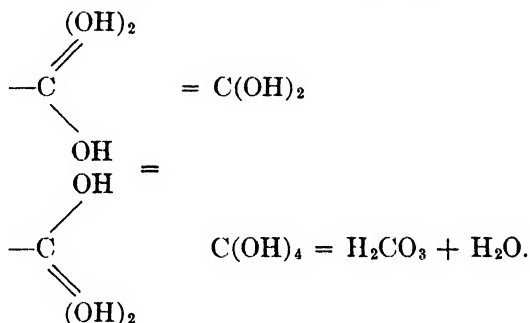
¹ Schilov: *Kolloid-Z.*, **62**, 107 (1930); Schilov and Tschmutov: *Z. physik. Chem.*, **148**, 233 (1930).

The second represents the typical case of surface saturation by hydroxyl groups:



In the presence of alkalis this behaves as an acid, neutralization follows and alkalis are adsorbed.

After autooxidation and reduction, or further oxidation by oxygen, carbon dioxide is split off and this reacts with the alkali to form a carbonate:



Thus, all phenomena resulting in alkali or acid adsorption can be explained by a simple assumption of the formation of hydroxyl groups upon the charcoal surface. The number of hydroxyl groups on each carbon atom determines the basic or acid nature of the oxide.

According to Bowden,¹ the significant area of a catalyst is not the arbitrarily defined maximum area, but it is that area which can be reached by the reactants. In the method of Bowden and Rideal² for measuring the areas of metallic surfaces by the electrolytic deposition of hydrogen from solution, the quantity measured is the amount of hydrogen which must be added to the surface to produce a definite change in the electrode potential.

Bowden and O'Connor³ have applied the same method using cathodes of fusible alloys (Wood's Metal). In addition, they determined the relation between electrode potential and current density. This relation gives the rate at which hydrogen is being evolved at the surface and is, therefore, a measure of the catalytic activity of the surface for the reaction. They find that for a solid this increases with rise in temperature, decreases when fusion begins, and

¹ Bowden: *Nature*, **122**, 647 (1928).

² Bowden and Rideal: *Proc. Roy. Soc.*, **120A**, 59, 80 (1930).

³ Bowden and O'Connor: *Proc. Roy. Soc.*, **128A**, 317 (1930).

increases again after complete fusion with further rise in temperature. Electrodes of metallic gallium rapidly catalyze the evolution of hydrogen and, therefore, relatively high current densities must be employed to produce a high hydrogen overvoltage. The accessible area of liquid gallium is about the same as that of mercury; on solidification the area increases to about 1.7 times the apparent area. According to the authors, the catalytic activity depends upon the accessible area and to a less extent upon the configuration of the surface metal atoms, but largely also upon the chemical nature of the metal.

Foresti¹ considers the surface covered by the adsorbed gas to be heterogeneous in that it is made up of active points of random distribution and different degrees of activity, and that this heterogeneous surface becomes homogeneous at low pressures. Using the data of Kistiakowski, Flosdorf and Taylor² for the adsorption of hydrogen on copper, he finds that the relation between the volume adsorbed and the pressure (0.03 mm to 0.3 mm Hg) is of the type, $V = K(p - m)^{1/2}$. If the constant m is neglected, the relation becomes quadratic, in which case, he contends, that the most active centers would be saturated by hydrogen atoms. This is not in harmony with the measurements of the differential heats of adsorption already made on the same samples of copper.

To become reactive, colliding molecules require a certain energy of activation. "The reducing factor for the case of three degrees of freedom is $-E/RT$, where E , the energy of activation is a magnitude of the order of some tens of thousands, (say 50,000 cal. per molecule. For a reaction at 1000° abs. the index is of the order of -24 .) Any cause which reduces the degrees of freedom by unity would reduce the index by one-third, a reduction of two degrees of freedom would reduce it by two-thirds of its value, and if all of the degrees of freedom were removed, the index would disappear entirely. With the above value of E the exponential factor in the several cases becomes (1) 3.77×10^{-11} , (2) 1.12×10^{-7} , (3) 3×10^{-4} and (4) unity, the first being the value met with in normal gas reactions.

Upon the basis of these relations, Porter³ states that "an adsorbed layer of oriented polar molecules with their proper poles all pointing outward toward a surrounding gas will tend to swing the colliding molecules round so that instead of it being a chance, it may become a certainty that suitable poles for reaction to take place will be presented to one another; in this case, the rate of reaction passes from the first to the second of the above categories and it is therefore increased in a ratio of about 30,000 and we have a reasonable case of catalytic acceleration. If, further, the forces exerted by an oncoming molecule could swing it round the axis of approach so that it inevitably "fits" its future partner, a second degree of freedom passes into the category of certainties and we have case (3) and the catalytic activity is multiplied by 10^9 , and so on."

"On the other hand, catalytic poisoning occurs when the wrong poles are made inevitably to present themselves. A single layer might be quite effective

¹ Foresti: *Gazz.*, **60**, 516 (1930).

² Loc. cit.

³ Porter: *Nature*, **126**, 349 (1930).

in stopping a reaction; and a much smaller quantity might reduce the rate a few hundred or thousand times."

Elements lying near the maxima of the Biltz atomic frequency-atomic weight curve are as a rule good catalysts. Srikantan¹ has attempted to correlate catalytic activity with the energy of vibration of the atom by means of the function, $4\pi M V r^2$, where M is the atomic weight, V the frequency and r is the amplitude of the atomic vibration at the melting point of the solid. It is found, in general, that elements with high energies of vibration like nickel, iron, osmium, platinum and carbon are active catalysts; they give high values for this function. Low values were obtained, however, for weak catalysts and for poisons such as chlorine, bromine, mercury, sodium and zinc.

In contact with heated palladium hydrogen undergoes important changes which appear in the form of an enhanced activity. According to Poljakov,² the subsequent recombination of the thus activated hydrogen should proceed with an emission of light. This conclusion was substantiated experimentally. He concludes that at the cost of energy, provided the palladium is not saturated with hydrogen, we can not only activate hydrogen, but also expel it into space in an active state. He has also shown that heat is liberated in the recombination of the hydrogen atoms at the glass walls.

Srikantan³ finds from a study of the interaction of carbon dioxide and hydrogen at various catalyst surfaces that a good catalyst support supplies the necessary energy at a lower temperature than a poor catalyst, and at the same temperature enables the reactants to attain an active state with a smaller quantity of energy.

Kröger⁴ has studied the quiet union of pure detonating gas in the presence of various catalysts. The catalysts used were, (1) those which adsorb oxygen markedly, such as silver, and (2) catalysts that act chiefly chemically, in which the adsorption is retarded by the formation of intermediate compounds (oxides). Catalysis with antimony, nickel, copper and the oxides of nickel and copper, involves the alternate oxidation and reduction of the catalyst metal. Using silver having a particle size of from 0.05 to 1.0 mm., he finds that the reaction takes place at a lower temperature, the greater the mass of catalyst taken. Further, for any given mass of catalyst the transformation increases slowly at first with rise in temperature, then more rapidly and, finally, at higher yields it increases more slowly with further rise in temperature. Quite similar results were obtained with nickel and nickel oxide. With copper oxide, however, temperatures of complete reaction are higher the greater the mass of the catalyst employed. Variation in the amount of powdered antimony used is without effect, indicating no adsorption of either hydrogen or oxygen.

¹ Srikantan: *Indian J. Physics*, **4**, 539 (1930).

² Poljakov: *Ber., Ukrain. wiss. Forschungs-Inst. physik. Chem.*, **2**, 55 (1930); See *Centralblatt*, **101**, 1822 (1930).

³ Srikantan: *Rec. Trav. chim.*, **49**, 1146 (1930).

⁴ Kröger: *Z. anorg. allgem. Chem.*, **194**, 73 (1930).

Adsorption

Schwab and Pietsch¹ have put forth a hypothesis to explain quantitatively not only the kinetics of catalysis, but also the phenomenon of activation and deactivation of the catalysts. The active points postulated by Taylor² are to be considered as homogeneous linear discontinuities of the catalyst surface, that is, as uni-dimensional boundaries of two-dimensional phases. These lines possess an enhanced heat of adsorption and, therefore, a diminished heat of activation. Adlineation implies an increased adsorption density on these linear structures. These lines may be due to crystal edges separating crystal surfaces of different crystallographic orientation, or to irregularities on the otherwise homogeneous surfaces produced either mechanically or by disturbances during crystal growth. The activity of these uni-dimensional phases may produce either orienting or deforming effects. That is, in the first case, they increase the speed of formation of the nucleus of the substance produced by decreasing the work required for the formation of the nucleus. In the second case, they make processes possible by decreasing the required heat of activation.

A number of experiments have been made recently³ demonstrating adlineation on crystal edges and points. In all of these the reactions are localized initially on the crystal edges and then they encroach progressively upon the crystal surface. The crystal edges and surface irregularities are assumed to be actually capable of playing the same pronounced energetic rôle which is ascribed to them in consideration of the theory of contact catalysis. They are the seat of catalytic activity whether in unicrystalline material or in the boundaries of polycrystalline substances.

Just how and where the adsorption of a solute does occur on a crystal lattice is a question which so far has been somewhat evasive. France and his co-workers⁴ have found that the growth ratios of potassium and ammonium alums are greatly modified when grown in the presence of dyes and other foreign substances. Thus, potassium alum grown in the presence of diamine sky blue grows into perfect cubes with no octahedral faces. Only the cubic faces are colored, and the growth ratio (100)/(111) changes from 1.60 to 0 in a dye concentration of 0.1 per cent. These effects are explained on the basis of the residual valency force fields of the crystal planes, of the interionic distances within the faces, and of the presence and distribution of polar groups in the adsorbed material. Further, the structure of the crystal is found to be a determining factor in the adsorption process. Only those faces covered by ions of like charge are colored by the dye. The cubic form of potassium alum crystals is made up of alternate layers of positive and negative ions,⁵ whereas in the octahedral form the layers contain both positive and negative ions. It

¹ Schwab and Pietsch: *Z. physik. Chem.*, B 1, 385 (1928); B 2, 262 (1929); *Z. Elektrochemie*, 35, 135 (1929).

² Taylor: *Proc. Roy. Soc.*, 108A, 105 (1925).

³ Pietsch, Kotowski and Berend: *Z. physik. Chem.*, B 5, 1 (1930).

⁴ France and his co-workers: *J. Am. Chem. Soc.*, 46, 540 (1924); *J. Am. Ceramic Soc.*, 10, 579, 821 (1927); 11, 579 (1928).

⁵ Wyckoff: *Am. J. Sci.*, 205, 209 (1923).

follows then that the dye should be adsorbed on the planes of the cube rather than on those of an octahedron. The position taken by the adsorbed dye molecules in the alum lattice is so far unknown.

Recently, Foote, Blake and France¹ have determined the lattice constants of pure potassium alum crystals and crystals grown in the presence of diamine sky blue. The lattice constants for the pure and dyed samples are found to be the same, showing that the adsorption of the dye does not measurably affect the plane spacings of the growing crystal. It appears justifiable to assume that the dye is adsorbed interstitially rather than as individual planes or by the replacement of ions of the unit cell.

Many investigations have been made in recent years dealing with the relation between adsorption from solution and the solubility of the substance adsorbed. In general, there appears to be an antibatic relation between adsorbability and solubility. In many cases these relations are quantitative.² Heyman and Boye³ have extended these studies to include the relation between adsorption and dielectric constant. To this end they have studied the adsorption of certain aliphatic acids, benzoic and picric acids, pyridine and triethylamine by ash-free charcoal from solutions in polar and non-polar solvents and in their binary mixtures. Although strict antibasic between dipole moments, as well as molecular polarization of the solvent, and adsorption does not always exist, the relation does hold, in general, when the solvents used are not too different chemically. Thus, in the homologous series of alcohols the adsorbability of the solute (benzoic and picric acids) decreases with increasing molecular polarization of the alcohol. Very distinct relations were obtained in the investigations employing binary solvent mixtures. The adsorption curves (percent adsorbed plotted against solvent composition) are directly related to the molecular polarization curves, P_{12} and P_2 , of the solvent mixture. Rectilinear adsorption curves are obtained not only when both solvent components are non-polar, but also when one component is polar, provided its specific polarization, P_2 , is not, or only slightly, changed by the non-polar solvent. However, when the specific polarization of the polar component (P_2 -curve) is strongly changed by the non-polar component, the adsorption curves are strongly curved. For example, when the P_2 -curve shows a maximum, the adsorption curve shows a minimum. The general character of the adsorption curves is dependent for the most part upon the nature of the solvent and not upon the nature of the adsorbate. The position of these maxima and minima vary from adsorbate to adsorbate. In general, the minima of the adsorption curves do not occur in the same solvent mixtures as the maxima of the P_2 -curves.

Alekseevskii⁴ has attempted to explain adsorption phenomena upon the basis of the distribution of valence forces in the complex molecular complexes of the adsorbent. According to their character, four types of valence forces

¹ Foote, Blake and France: *J. Phys. Chem.*, **34**, 2236 (1930).

² Freundlich, *Kapillarchemie*, IV, 1; Lundelius: *Kolloid-Z.*, **26**, 245 (1925); Angelescu and Comanescu: **44**, 288 (1928); Sata: **49**, 275 (1929); Herz and Levi: **50**, 21 (1930).

³ Heyman and Boye: *Z. physik. Chem.*, **150 A**, 219 (1930).

⁴ Alekseevski: *J. Russ. Phys.-Chem. Soc.*, **62**, 817 (1930).

are to be distinguished. These are: the homopolar type found in the molecules of elementary substances; the heteropolar stable compounds of different elements, like H_2SO_4 , NaCl ; the third type leading to molecular association, or crystalline hydrate formation; the fourth type represents the valence forces present in unstable compounds, that is, the forces in adsorption compounds. Only the last type of valence forces, which are distinguished by variable characteristics, are capable of solving adsorption phenomena. Upon the basis of these considerations, Alekseevskii has deduced constitutional formulae for active charcoal, silica gel, and clays.

Dohse and his co-workers¹ have applied their previous method to the hydrogenation of C_2H_4 at 0° , with nickel supported by activated charcoal as the catalyst. C_2H_4 and C_2H_6 are both strongly adsorbed, the hydrogen only weakly adsorbed by the catalyst. They applied equi-molecular quantities of C_2H_4 and H_2 . By allowing the former to form a film upon the surface and then permitting the H_2 to enter they found the reaction to proceed specifically as a first order reaction, although two molecules are taking part. While the reaction velocity is independent of the C_2H_4 concentration it is directly proportional to that of the hydrogen. The reaction is of zero order when the concentration of the hydrogen is kept constant. They assume the existence of a two-dimensional gas layer on the support surface in which the ratio of C_2H_4 to H_2 is relatively large. When a molecule of hydrogen strikes upon a nickel point it becomes activated and reacts with the C_2H_4 molecule. Since its adsorption potential is practically the same toward nickel and charcoal, the C_2H_4 molecule formed moves laterally to the charcoal from which it vaporizes. Hitherto, the activity of the contact has been assumed to be dependent upon the magnitude of the active surface and the activity of the individual active points. According to the authors, the inactive support surface plays an important rôle in catalytic processes. It forms not only the reservoir from which the active points are supplied, but also a space into which the newly formed molecules are transported from the active points with little work. For, if the molecules had to be transferred directly to the gas phase, the reaction would take place much more slowly because of the much greater potential difference between the active point and the gas phase than between the active point and the inactive surface.

According to McBain and his co-workers,² the ordinary empirical sorption formula, $x/m = kp^{1/n}$, fails completely for the sorption of organic vapors by activated sugar charcoal. At the lowest pressures it gives a flat curve instead of the required straight line when plotted on a logarithmic diagram, the curve changing suddenly into a nearly horizontal line for all the higher pressure ranges. The authors assert that the only adequate expression for sorption results is that of Langmuir, namely $x/m = ab.p/(1+a.p)$, where a and b are constants. This, when rearranged gives $\frac{p/p_0}{x/m} = \frac{1}{ab} + \frac{p/p_0}{b}$, which is the

¹ Dohse and his co-workers, Kälberer and Schuster: *Z. Elektrochemie*, **36**, 677 (1930).

² McBain, Jackman, Bakr and Smith: *J. Phys. Chem.*, **34**, 1439 (1930).

equation of a straight line, if we plot $\frac{p/p_0}{x/m}$ against p/p_0 . The Langmuir formula presupposes the validity of Henry's law at sufficiently low pressures, where $1/n$ should equal unity, and they found this to be actually true experimentally. Although the vapors are very similar in physical properties, their sorption by the same charcoal is very different. At the lowest pressures the non-polar hexane is the one most sorbed, and it approaches saturation, whereas the polar methanol does not. With change in pressure the sorption of methanol is more rapidly adjusted than that of hexane. They conclude also from their results that heats of adsorption cannot be calculated by means of the van't Hoff isochore, unless there is some certainty that in the isotherms at different temperatures the impurities present have exerted a precisely similar effect.

Improvements in evacuation have been found¹ to change not only the position of the adsorption isotherms, but also their form. Only by carefully and completely outgassing the charcoal at high temperatures, then admitting the vapor to be adsorbed and again outgassing at high temperatures is it possible to obtain a charcoal which is free from foreign materials. The adsorption isotherms obtained with this charcoal are of an entirely new type, in that almost all of the adsorption occurs at low pressures. There is practically no further adsorption with increase in pressure. The more drastic the preliminary treatment, the lower is the pressure necessary for complete saturation.

At very low temperatures and for a given pressure the adsorption of hydrogen on nickel is relatively large. It passes through a minimum between -200° and -175° , rising to a maximum at about -100° and then falls off gradually again with increasing temperature. The magnitude of the minimum is dependent upon the pressure. At 600 mm. the adsorption is independent of the temperature for temperatures between -110° and 0° , a fact which is explained by the assumption of a completely saturated surface layer. Except for the interval, -191° to -183° , where adsorption is discontinuous, the adsorption is, in general, reversible and reproducible. Benton and White² assume that the adsorption at the lower temperatures is of a "secondary" type, that is, more of a molecular nature, while at higher temperatures a relatively greater part of the nickel surface is capable of holding hydrogen by adsorption of a "primary" type, involving a marked activation of the gas.

Garner and Kingman³ find that hydrogen or carbon monoxide is adsorbed reversibly on oxide surfaces at ordinary temperatures and adsorbed irreversibly at higher temperatures. The gas adsorbed at equilibrium pressures of 10^{-3} to 10^{-4} mm. on a $\text{ZnO-Cr}_2\text{O}_3$ catalyst is liberated at 100° to 120° , but is readsorbed within thirty minutes, giving a high vacuum. With further rise in temperature no gas is given off until 350° when water and carbon dioxide are evolved. Mixtures of hydrogen and carbon monoxide behave in a similar manner. The reduction of oxides by either of these gases is assumed to pro-

¹ McBain, Lucas and Chapman: *J. Am. Chem. Soc.*, **52**, 2668 (1930).

² Benton and White: *J. Am. Chem. Soc.*, **52**, 2325 (1930).

³ Garner and Kingman: *Nature*, **126**, 352 (1930).

ceed in three stages: an adsorption of the gas, then a combination with the surface atoms and, finally, the desorption of water, or of carbon dioxide, depending upon the starting gas.

When used alone, or mixed with other oxides, MnO_2 is a very active oxidizing catalyst. Its activity, however, appears to be influenced strongly by the alkalinity of the medium in which it is prepared and, hence, by the amount of alkali adsorbed by the oxide. Working with four differently prepared samples of MnO_2 and with a mixed catalyst containing 37 per cent of silver oxide, Lanning¹ finds that the adsorption curves for water vapor and carbon dioxide do not differ materially from the curves for oxides prepared in the absence of added alkali. He states that the effect of the alkali in depressing the catalytic activity of these oxides cannot be due to a change in the physical structure of the oxide, but must be due rather to catalytic poisoning by the adsorbed alkali.

Foote and Dixon² have studied the adsorption of water and benzene vapors on MnO_2 . The isotherms for both vapors at low pressures indicate that these vapors are adsorbed in the same way that the permanent gases are adsorbed by charcoal. Pure surface adsorption is assumed within the range of pressures used. When the value of p/p_0 is about 0.5 the isotherms break rather sharply and the amount of vapor absorbed increases rapidly with a small increase in pressure. One part of the water isotherm corresponds to an adsorption, the other to condensation in the capillaries. Polanyi's adsorption theory is confirmed. Treatment of the outgassed oxide with CO or CO_2 diminishes strongly the surface adsorption, but does not alter the capillary adsorption. Both gases cover the active adsorption patches, reducing the surface adsorption of water vapor. Oxygen is without effect. Removal of these gases by heating restores the surface adsorption of water to its normal value.

Alekseevskii³ finds that the optimum temperature of ignition of alumina for the adsorption of ethyl and isoamyl alcohol vapors is $400^\circ\text{--}420^\circ$; for the adsorption of ethylene and ethylenic hydrocarbons and benzene is $600^\circ\text{--}620^\circ$.

The catalytic activity of samples of similarly prepared cubic and rhombohedral ferric oxide (Fe_2O_3) toward the oxidation of benzidine or guajac resin by hydrogen peroxide is practically the same. It is not a function of the crystal structure of the two oxides.⁴ Several hours heating at 550° practically destroys their catalytic activity toward these oxidations. As measured by the rate of combination of an oxygen-hydrogen mixture on their surfaces the activities are approximately the same, but in this case heating does not alter the activity of either toward this reaction. The decomposition of ozone at -74° follows equally rapidly on both forms, but less rapidly on the highly heated oxides than on those dried at 300° . In their water sorption capacities, however, they exhibit distinct differences, that on the cubic Fe_2O_3 being from 10 to 60 percent less than on the rhombohedral form. The sorption capacity

¹ Lanning: *J. Am. Chem. Soc.*, **52**, 2411 (1930).

² Foote and Dixon: *J. Am. Chem. Soc.*, **52**, 2170 (1930).

³ Alekseevskii: *J. Russ. Phys.-Chem. Soc.*, **62**, 221 (1930).

⁴ Emmett and Love: *J. Phys. Chem.*, **34**, 41 (1930).

of both forms is greatly diminished by heating to 550° and is not again restored by activation with hydrogen-oxygen mixtures. The most plausible explanation for the loss of catalytic activity of both forms is sintering.

When hydrogen-free naphthas are passed over initially sulfur-free nickel catalysts¹ at 300° the first portions passing the catalyst contain very little sulfur. The sulfur content of the product increases rapidly at first, then more and more slowly, finally attaining a constant sulfur content after a sufficient quantity of liquid has been vaporized through the catalyst. The reduction of the sulfur content is dependent upon the naphtha employed, the differences exhibited by the different naphthas being assumed as due to the nature and reactivity of the sulfur compounds present. Hydrogen-free naphtha vapors yield no hydrogen sulfide until the steady state of constant sulfur content is attained. It then increases slowly and finally reaches a constant state which then continues as long as the catalyst is used. All mercaptans are nearly completely removed in a single passage of the vapor through the catalyst at the steady state. Other sulfur compounds, like propyl sulfide, are also decomposed.

Sulfur-free nickel catalysts completely remove all sulfur from naphthas in the form of vapor. With continued use the nickel catalyst becomes less efficient in its action, but it finally reaches a steady state when its effectiveness in reducing sulfur compounds becomes constant.

Addition of hydrogen to the naphtha vapor increases the effectiveness of the catalyst in removing sulfur. The evolution of hydrogen sulfide begins at the beginning of the run. The evolution increases somewhat as the steady state is approached and then remains constant.

Although considerably less effective than nickel, the iron catalyst exhibits the same type of behavior. At no stage, however, does iron completely remove the sulfur.

Experiments made on the adsorption of sulfur from the liquid phase showed that the amount of sulfur removed is proportional to the quantity of catalyst added until the sulfur content of the naphtha has been reduced to a certain value. The sulfur is irreversibly adsorbed and it is not removed by benzene or sulfur-free naphtha. While all mercaptan sulfur is not adsorbed, other sulfur compounds are adsorbed.

The results of the work of Elgin, Wilder and Taylor show that the nickel sulfide surface catalyzes the removal of sulfur by catalyzing the decomposition of certain sulfur compounds with the evolution of hydrogen sulfide. The function of hydrogen in increasing the efficiency of the catalyst seems to be to maintain some fraction of the surface free from sulfur.

Employing the same technique with nickel contacts, Elgin² has continued the study of the action of a nickel catalyst on pure sulfur compounds when present individually in naphtha. Both butyl mercaptan and thiophene are at first removed when, in the absence of hydrogen, the vapors are passed over sulfur-free nickel at 300° . The catalyst reaches a state of constant activity in which it catalytically decomposes practically the entire mercaptan content

¹ Elgin, Wilder and H. S. Taylor: *Ind. Eng. Chem.*, **22**, 1284 (1930).

² Elgin: *Ind. Eng. Chem.*, **22**, 1290 (1930).

with the liberation of hydrogen sulfide. It does not, however, affect the thiophene after the initial stages of the run. Nickel catalysts which have been carried to the state of constant activity with butyl mercaptan catalytically decomposed all of the other sulfur compounds used, (mercaptans and sulfides), except thiophene. Hydrogen sulfide is evolved when hydrogen is added to the naphtha solutions of all of the sulfur compounds. Even thiophene is removed at 300° when in contact with the catalyst at the steady state. Increasing the temperature to 400°, or increasing the proportion of hydrogen to naphtha increases the amount of sulfur removed. According to Elgin, the decomposition of the mercaptans follows the reaction,



From the results of a series of investigations of the adsorption of electrolytes by activated charcoal, Frumkin¹ is inclined to look upon active charcoal as a gas electrode. At the cost of adsorbed gases it sends ions into solution, thereby assuming a definite charge and attracting ions of opposite sign. In this way there is formed an electric double layer and the concentration changes in the solution resulting from the formation of this double layer are to be considered as adsorption. Ash-free charcoal activated at high temperatures adsorbs acids from neutral salt solutions, leaving the solution in contact with the charcoal strongly alkaline. The same charcoal adsorbs free acids intensively, but it does not adsorb the strong bases. Frumkin assumes in this case that the charcoal functions as an oxygen electrode.

On the basis of these considerations, it is obvious that if a charcoal is sufficiently heated at a high temperature to remove all traces of adsorbed gases, it cannot function as an electrode and send ions into solution. For this reason the adsorption observed on gas-charged charcoals will be impossible. Outgassed charcoal activated at 1000° in an atmosphere of carbon dioxide does not adsorb electrolyte material when brought in contact with dilute solution of hydrochloric acid or of sodium hydroxide. If air is admitted to the vessel containing the outgassed charcoal immersed in an aqueous solution of the acid or of a salt, the charcoal again assumes its original adsorption capacity. Further, if the proper quantities of acid and charcoal are used, the acid will completely disappear from the solution.

As pictured by Frumkin, the mechanism of the adsorption process consists of the formation of hydroxyl ions from the adsorbed oxygen; these pass into solution, leaving a positive charge upon the charcoal surface:



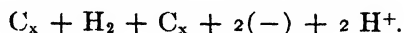
In an acid solution the OH⁻ ions combine with the H⁺ ions of the solution while the positive surface attracts the anions of the solution and, thus, the acid disappears from the solution. Under similar conditions, neutral solutions become alkaline because the anions of the solution are replaced by OH⁻ ions. According to this view, alkaline solutions should not, and they do not,

¹ Frumkin: *Kolloid-Z.*, 51, 123 (1930); see also Bruns and Frumkin: *Z. physik. Chem.*, 147 A, 125 (1930).

exhibit any appreciable concentration changes in contact with oxygenated charcoal. Under the conditions employed the amount of acid adsorbed is equivalent to the oxygen-content of the charcoal.

The oxygenated charcoal electrode is far from reversible, its potential being several decivolts less than that of a reversible oxygen-electrode. The oxygen potential of the charcoal may be increased to that of the reversible oxygen-electrode by platinizing the charcoal. The acid adsorption is strongly increased by the presence of the platinum.

There is a complete reversal of the adsorption behavior when the oxygen-charged charcoal is heated for some time in an atmosphere of hydrogen and then placed in an air-free electrolyte solution. The charcoal now adsorbs alkali, but no acid, and the neutral solution in contact with the charcoal becomes acid. The charcoal now sends hydrogen ions into solution at the cost of the adsorbed hydrogen, leaving the charcoal with a negative charge to attract the positive ions of the solution. Schematically, the mechanism is



The amount of hydrogen disappearing is equivalent to the amount of hydrogen ions formed, and, therefore, to the alkali adsorbed.

It is interesting to note also the application of Frumkin's views to the stability of charcoal suspensions. Oxygen-charcoal in alkaline solutions and hydrogen-charcoal in acid solutions are only weakly charged because of the presence of the opposing OH^- and H^+ ions, respectively; the corresponding suspensions coagulate rapidly. Oxygen-charcoals in acid solution and hydrogen-charcoals in alkaline solution are, on the contrary, highly charged and give stable suspensions. The influence of polyvalent ions is in accord with the demands of the theory. Polyvalent anions coagulate oxygen-charged platinized charcoal particles and polyvalent cations stabilize them. Exactly the reverse is true for the hydrogen-charged particles.

Sugar charcoal activated at 500° adsorbs¹ mineral acids from solutions of equivalent concentration in the order, $HCl > H_2SO_4 > H_3PO_4$, and organic acids in the order propionic > valeric > heptylic. Activating the charcoal at 800° reverses the order of adsorption of these acids. Activation in air decreases the adsorption of iodine from potassium iodide solution and increases the adsorption of alkali. Activation in carbon dioxide, on the other hand, increases the adsorption of iodine, but does not affect that of the alkali. Heating the charcoal in vacuo at 1200° removes carbon dioxide from the surface and thus destroys its ability to adsorb alkali. By this treatment the ability to adsorb acids is decreased, but the amount of iodine adsorbed is practically unchanged. Activation increases the pore size, allowing the larger molecules access to more surface. The amount of larger molecules adsorbed per unit mass of adsorbent is thereby increased in greater proportion than that of the smaller molecules.

¹ Dubinin: *Z. physik. Chem.*, A 150, 145 (1930).

According to Brouckère,¹ the adsorption of alkali iodides by barium sulfate is strictly reproducible only in the dark and in the absence of oxygen. The anomalies arising are due to the selective adsorption of the iodide ion. In experiments with solutions of potassium iodide containing free iodine, more atoms of iodine are adsorbed than of potassium, the ratio, I/K, being always approximately 3. It appears then as if the adsorption depends almost solely upon the KI₃ compound. The isotherms obtained in the iodine-free potassium iodide and in those containing no free iodine appear to indicate that, *ceteris paribus*, the KI₃ complex is more strongly adsorbed than is the simple iodide KI.

A polished brass foil immersed in a dilute solution containing sodium thiosulfate and lead acetate upon heating to boiling assumes a bright golden yellow color. The color then passes successively through a series of colors, namely, reddish violet, deep blue, bright steel blue and, finally, to gray. Copper, silver and iron show similar color changes. Beutel and Kutzelnigg² find that when the clear colorless solution of the complex lead thiosulfate is heated to boiling it becomes turbid and of a blue color. After a few minutes there is formed an apparently amorphous precipitate consisting of irregular granules. Upon longer boiling the lead sulfide is deposited as a mirror. The coloring of metals consists in the adsorption of insoluble compounds formed by the decomposition of the complex salt. Adsorption on metal surfaces can be considered as a special case of general surface adsorption. That it is of an electrochemical nature is shown by the following illustrations. Of the sixteen metals studied, Al, Mn, Zn and Cr, all standing above iron, did not color. All of those following iron, except cadmium and platinum did color during the treatment. Of the series, copper, silver, lead, and gold, the coloring is slower the more noble the metal. If a copper or zinc wire is used in place of the binding string, then the platinum also colors. The other metals also color more quickly and the time required to produce a given color is much shortened. The time required is much shorter with zinc than with copper wires. Further, the time required to produce a given color decreases with rise in temperature.

Kosakewitsch and Ismailow³ find that the adsorption of phenol from aqueous solutions and of benzoic acid from solutions in methyl and ethyl alcohol by charcoal is increased by alkali halides, the magnitude of adsorption increasing with the salt concentration. The activity of the adsorbate is increased by the salt. The relation between the adsorption of phenol and its activity in the solution is most clearly shown when the values of x/m are plotted against the activity of the phenol instead of the concentration. When this is done the adsorption curves for the pure water and the salt solutions coincide throughout. It is possible, therefore, to calculate the relative activity of easily adsorbable substances from adsorption data. By attributing the neutral salt effect to solvation they were able also to calculate values for the

¹ Brouckère: *Bull. Soc. chim. Belg.*, **39**, 174 (1930).

² Beutel and Kutzelnigg: *Z. Elektrochemie*, **36**, 523 (1930).

³ Kosakewitsch and Ismailow: *Z. physik. Chem.*, A **150**, 295 (1930).

hydration per mol of salt which are in good agreement with values obtained by other methods.

Alekseevskii and Musakin¹ have studied the effect of a large number of acids upon the adsorptive power of various wood charcoals. Perchloric acid increases the adsorption of methylene blue and Congo red; it with chromic acid, nitric acid, and bromine water enhance the adsorption of phenol. The most active adsorbents for acetylene from the air were obtained by treatment of the charcoals with nitric and perchloric acids and bromine water. Treatment with nitric, perchloric, hydrofluoric, and chromic acids give the best adsorbents for benzene vapor. In general, the adsorptive properties of wood charcoal appear to be enhanced by the action of volatile oxidizing substances.

Heat of Adsorption

In a study of the relation between particle size and catalytic activity of three platinum blacks, prepared by different methods, Taylor, Kistiakowski and Perry² found that the two samples having the smaller particle size showed the greater catalytic activity. One of these was found to be superior in oxidation reactions, and the other slightly better for hydrogenation. The effect of extended heat treatment on the adsorption capacity of the three samples was quite marked. Heating to 350° gradually destroyed the adsorptive capacity of the sample of large size, reducing the adsorption of hydrogen practically to zero and that of oxygen nearly as much. The sample showed much sintering and was almost a metallic gray in color. The two samples of smaller size withstood a similar heat treatment much better, and, although somewhat sintered, they retained their black color practically unchanged. These sintering effects appear quite anomalous in view of the higher surface energy of the particles of smaller size. They found a distinct parallelism between catalytic activity and physical properties. The poorest catalyst has the coarsest structure and is the poorest adsorber. The quantities of hydrogen adsorbed and the heats of adsorption of hydrogen parallel the catalytic activity of this catalyst in the hydrogenation of ethylene.

Taylor, Kistiakowski and Perry³ have also determined the differential heats of adsorption of H₂, O₂, SO₂, and CO on the same three differently prepared platinum blacks. The curves for the differential heats of adsorption show no minima. They state that the minima so frequently observed by others must be considered as a phenomenon specific for the adsorbent and adsorbate. The striking feature of their results is the magnitude of the heats of adsorption. These attain values of 30000 cal. and more for H₂, SO₂, and CO, and greater than 100000 cal. for oxygen. These values are, however, in harmony with those obtained by others. Langmuir⁴ estimates the heat of adsorption of carbon monoxide to be of the order of 30000 cal. According to him, carbon monoxide begins to leave the surface in a vacuum at 350°-400°.

¹ Alekseevskii and Musakin: *J. Russ. Phys.-Chem. Soc.*, **62**, 205 (1930).

² Taylor, Kistiakowski and Perry: *J. Phys. Chem.*, **34**, 748 (1930).

³ Taylor, Kistiakowski and Perry: *J. Phys. Chem.* **34**, 799 (1930).

⁴ Langmuir: *J. Am. Chem. Soc.*, **40**, 1361 (1918).

whereas oxygen can not be removed below 1200° . Its heat of adsorption should, therefore, be much higher than that for carbon monoxide.

Flosdorf and Kistiakowski¹ have determined the heat of adsorption of hydrogen on zinc-chromium oxide, and of hydrogen, oxygen and water vapor on supported and non-supported platinum catalysts. While a fresh sample of the zinc-chromium oxide adsorbs very little hydrogen at 0° , it adsorbs large quantities at 100° . The adsorbed hydrogen could not be removed from the oxide surface by pumping at higher temperatures, except in the form of water. When heated in hydrogen at 100° or at 300° until no further gas was taken up there resulted a green material due undoubtedly to the reduction of the oxide. The green material obtained at 300° proved to be a reversible and strong adsorbent for hydrogen. The adsorption on the reduced sample was now stronger at 0° than at 100° , and on heating the sample to 400° the adsorbed hydrogen was recovered quantitatively. The heat of adsorption on the fresh, unreduced samples was 60000 cal. per mol of hydrogen, while that on samples reduced at 300° was 20000 cal. or less. These results seem only to emphasize the futility of attempting to measure heats of adsorption of hydrogen on easily reducible oxides. The higher value obtained represents largely the heat of reduction of the chromium oxide. They find that the heat of adsorption of water vapor on platinum measured directly is in good agreement with that calculated from the data on the adsorption of hydrogen and oxygen.

With the view of ascertaining whether the absence of a maximum heat of adsorption is dependent on certain conditions, including those employed by previous investigators, or whether with this metal the form is general, Maxted² has redetermined the heat of adsorption of hydrogen on platinum at 0° and 20° . He finds, in general, that the total heat evolved during the acquisition of a given adsorbed hydrogen content decreased with the age of the catalyst and finally approached a rather steady value. The differential heats of adsorption pass through well-defined maxima, the maxima becoming less pronounced with ageing of the catalyst. While the curves for the different series were found to be similar, the actual curve obtained for a given sample of platinum is dependent upon its history and degree of outgassing. Hence, the relatively high temperatures, 250° to 300° , employed by Taylor, Kistiakowski and Perry³ may possibly account for the non-observance of a maximum. The adsorption isotherms were found to exhibit a gradual shift with time toward the pressure axis. "It would appear then that the heat of adsorption and the hydrogen isotherms are properties which, like catalytic activity, are specific not only to an individual specimen of a hydrogenating catalyst, but also to its condition and history." Maxted concludes that the possession of a high differential heat of adsorption and high primary adsorption should be intimately related to the possession of a relatively high catalytic activity. And this for the reason that it would be expected that a given point on the catalyst

¹ Flosdorf and Kistiakowski: *J. Phys. Chem.*, **34**, 1907 (1930).

² Maxted: *J. Chem. Soc.* 1930, 2093.

³ Taylor, Kistiakowski and Perry: *Loc. cit.*

surface must possess at least a certain critical free energy to bring about, by adsorption, the activation of hydrogen and, consequently, catalysis.

In a study of the adsorption of SO_2 by charcoal at 0° and 5° and in the region of small adsorbed masses, Polanyi and Welke¹ have found that the isotherms, as well as the curves for the differential heats of adsorption calculated from them, show a very peculiar and hitherto unrecognized course. The isotherms show two flexion points, the molar heat of adsorption passing through a minimum at about 6500 cal. and then rising to over 10000 cal. Since such a course, if true should be of the greatest theoretical interest, Magnus, Giebenhain and Velde² have tested its reality by a series of new measurements. In this they determined the integral heat of adsorption of SO_2 on coconut charcoal for the concentration range of 13 to 17000 micromols, on 15.75 g. of charcoal (0.05 to 68 mg. of gas to 1 g.). They find that the molar heat of adsorption shows a regular retarded decrease with increase in the amount adsorbed. Approximate differential heats of adsorption were obtained by the admission of about 30 micromols to the already more or less charged charcoal. Only above an adsorbed mass of 2000 micromols to 1 g. of charcoal do the curves thus obtained agree within limits of experimental error with those calculated from the integral heats. For lower amounts adsorbed, the experimentally determined differential heats are much greater than those calculated. These deviations have been explained qualitatively on the basis of the time necessary for the adjustment of adsorption equilibria in the capillaries.

Dixon³ has found that the heat of adsorption, q , in cal. per mol adsorbed, can be expressed in terms of the adsorption potential, ϵ , and the amount adsorbed, x , by means of the relation,

$$q = \int_0^{\text{total}} \frac{\epsilon dx}{x},$$

Hence, the calculation of the heat of adsorption at any desired pressure involves merely the plotting of ϵ against x , finding the area under the curve and dividing this by the amount of gas adsorbed. Basing his calculations on data previously obtained⁴ he finds the differences between the calculated and observed heats of adsorption to range from 2600 to 3200 cal. per mol. These differences represent the heats of condensation of carbon dioxide.

The Polanyi theory accounts only for the heat liberated in compressing the gas from the free state to the state in which it exists upon the charcoal surface. The heat of condensation of carbon dioxide at 0° under its own vapor pressure is 2420 cal. per mol. As the temperature falls the space volume of the liquid diminishes and that of the heat of condensation increases. Since the major portion of the carbon dioxide adsorbed exists at a density greater than that of the normal liquid at 0° , Dixon assumes that the gas condenses to

¹ Polanyi and Welke: *Z. physik. Chem.*, **132**, 371 (1928).

² Magnus, Giebenhain and Velde: *Z. physik. Chem.*, A **150**, 285 (1930).

³ Dixon: *J. Phys. Chem.*, **34**, 870 (1930).

⁴ Magnus and Kalberer: *Z. anorg. allgem. Chem.*, **164**, 345 (1930).

a liquid whose density and heat of vaporization are greater than that of the normal liquid. In this pressure range the adsorption forces are very strong and, therefore, the equation of state employed in developing the theory no longer applies. It should be expected then that in the presence of the existing strong force fields the heat of adsorption should be higher than that calculated by means of the normal equation of state. The Polanyi theory postulates a compression of the gas on the surface of the adsorbent. The calculations of Lowry and Olmstead¹ and those of Dixon show that this theory agrees well with the experimental data obtained.

Unimolecular Films

Within recent years Lyons and Rideal² have made a critical study of the properties of unimolecular films. The force-area curves of palmitic acid on the surface of solutions of varying pH show that the high pressure region of the curves is practically independent of the nature of the underlying solution. It increases, however, very slightly in steepness with increasing alkalinity, although the area remains unchanged at zero compression. Spreading proceeds slowly on acid solutions, the rate of spreading increasing rapidly with increase in pH; in very strongly alkaline solutions equilibrium is practically instantaneous. They suggest that the attraction of the molecules for acid surfaces is very small.

The expansion of the film is believed to be due to a gradual tilting of the molecules from the close-packed formation of the solid state. The solid condensed film consists of molecules tilted to such an angle that the zig-zag chains interlock. It is assumed that in liquid condensed films the molecules are free tilted, but, in general, oriented parallel to one another, giving a two-dimensional structure analogous to the smectic state of mixed crystals. The expanded state is regarded as a two-dimensional liquid. The gradual transition from the solid condensed film through the liquid condensed and expanded films to the vapor film is due to the gradual increase in the angle of tilt of the film molecules as their mutual attraction becomes weakened in comparison with the attractive forces between the chain and the surface.

Upon solution the film area is reduced slowly at constant pressure. The rate of decrease is appreciably increased by increasing the alkalinity, by increasing the temperature, and to a slight extent also by increasing the pressure. If the film pressure is kept constant on solutions of pH 8.5-13.0, complete solution does not occur, but some form of relatively insoluble film is left. This new form of film is regarded as a bimolecular leaflet, like the elementary leaflet in a soap bubble; it contains palmitic acid and sodium palmitate. On weakly alkaline solutions the lower layer of the bimolecular film is less closely packed than the upper, but the closeness of the packing increases with increase in alkalinity. The solution of a unimolecular film begins at nuclei formed by the adsorption of soap molecules beneath the surface, so that when

¹ Lowry and Olmstead: *J. Phys. Chem.*, **31**, 1601 (1930).

² Lyons and Rideal: *Proc. Roy. Soc.* **124A**, 322, 333 (1929); **128A**, (1930); *Nature* **125**, 351, 455 (1930).

there is initially no soap in the bulk of the solution the process is autocatalytic.

Light reflected by soap bubbles shows at first the continuous color of the ordinary soap lamella, then the lamella begins to vibrate and the liquid collects in minute spheres. At the same time areas of unit color appear; these are separated by circles and give a mosaic appearance to the lamellae. That the areas are liquid is shown by the fact that their boundaries are perfect circles, and that these boundaries may be displaced without destroying the lamellae. The detached droplets also show the Brownian motion.

Perrin¹ believes that the thickness of each layer in the liquid lamellae is a whole-numbered multiple of the same elementary layer thickness. That is, the elementary structures are formed by the superposition of a number of identical lamellae having a thickness of 4.4 millimicrons. With increasing thickness of the film the order of color in white light increases, thus showing the discontinuous and periodic structure of the material. These films show black spots by reflected light. These spots consist of thin films of water molecules which are surrounded on all sides by adsorbed oleic acid or oleate molecules with their acid groups dissolved in the water. The structure forms are anisotropic lamella or liquid crystal layer.

It has been found² that in the formation of the adsorption film at the interface air-solution of a surface active substance the surface tension does not change, if the concentration of the substance is very small. According to Talmud and his co-workers, this corresponds to a state in which the polar molecules lie horizontally and unoriented upon the surface of the water. Hence, they assume that the polar groups of the surface active substances are only slightly hydrated because of the inhibition of the predominating hydration of the polar groups of the molecules by the non-polar chains. With further increase in concentration of the surface active substance, and simultaneous with the beginning of the decrease in surface tension, there is a partial orientation of the polar molecules in the adsorption layer which is accompanied by a greater hydration of the polar groups. In the saturated adsorption film, where the molecules are completely oriented and the surface tension attains a minimum value, the polar groups are all hydrated. They conclude that in the layer consisting of non-oriented, horizontally lying molecules, the hydration of the polar groups is a minimum. Also, that the hydration of the polar groups is a minimum in the saturated film in which the completely oriented molecules stand perpendicularly to the surface. Consequently, the maximum hydration of the polar groups must occur at some intermediate concentration of the surface film. In this narrow range of maximum hydration of the polar groups the polar molecules are only partially oriented, that is, they are inclined at a certain angle to the surface. With respect to thermal agitation they behave not as a two-dimensional crystal of the saturated adsorption phase, but as a meso-phase,—a two-dimensional liquid crystal. Such

¹ Perrin: *Kolloid-Z.*, **51**, 1 (1930).

² Talmud: *Evolution of the Theoretical Views on the Nature of the Flotation Process, Non-Ferrous Metals*, No. 1, 68 (1930) (In Russian); Talmud and Suchowoloskaja: *Z. physik. Chem.*, (in press); Talmud, Suchowoloskaja and Lubman: *A* **151**, 401 (1930).

considerations must lead to the view that in the region of maximum hydration the chains of polar molecules, by intertwining, must form a system analogous to a lyophile gel, a system which exhibits mechanical rigidity toward dislocation. The longer the chain and the greater its complexity, the greater will be the rigidity of the surface film. Further, the greater the solubility of the molecule the less will be the rigidity in the region of maximum hydration. In measure as the molecules assume a more vertical orientation and the molecules become less hydrated, the firmness of the adsorption film will decrease. It will reach a zero value for the liquid film and a definite constant rigidity for the adsorption film.

Monomolecular layers of fatty acids upon a water surface are analogous to a two-dimensional or "surface" gas. This gas exerts a definite pressure per unit length. For small concentrations the molecules are widely separated and obey the three-dimensional gas law, $PS = RT$, where P is the pressure and S is the surface. At greater concentrations the attractive force between the molecules becomes effective and there is formed finally a condensed film or two-dimensional liquid. According to Semenov,¹ the two-dimensional gas behaves like an ordinary three-dimensional gas and should, therefore, adapt itself to the van der Waals equation.

With increase in pressure, P , surface liquid formation occurs and the whole adsorbed layer separates finally, at high pressures, into a two-dimensional liquid and a saturated surface vapor phase. The liquid surface forms the more easily the greater the forces of attraction prevailing between the molecules. These are particularly large between metallic atoms, and, therefore, we should expect the formation of the surface liquid phase to occur easily with metal vapors.

Semenov's theory shows the existence of an inversion temperature, T_i , below which the critical condensation pressure exceeds, and above which it is less than the saturated vapor. In the temperature range, $T < T_i$ and at pressures below the critical, the amount of adsorbed gas increases with the pressure and forms a two-dimensional gas phase on the surface. When the critical pressure is reached a liquid is formed which quickly covers the whole surface; with this there is an accompanying decrease of the outer gas pressure to P_g . For the range $T > T_i$, and at pressures less than the critical, we find the same behavior, but in this case the unimolecular liquid layer formed when the pressure reaches the critical pressure, is stable, since it is less than p_g . As the pressure, p , is increased, the formation of a second liquid layer begins. At a certain pressure there is a stable bimolecular adsorbed layer. Thus multi-molecular adsorption occurs only when $T > T_i$ and $p_{crit} < p < P_g$.

Hydrogenation

Balandin² presents an empirical rule by which it is possible to predict the products of hydrogenation of organic substances. By assigning to the elements, halogen, oxygen, nitrogen, and carbon, the numbers 1, 2, 3 and 4,

¹ Semenov: *Z. physik. Chem.*, B 5, 471 (1930).

² Balandin, *J. Russ. Phys.-Chem. Soc.*, 62, 703 (1930).

respectively, and letting π represent the product of the numbers assigned to any pair of these elements, he finds that the ease with which the linkage between the two elements is broken in the catalytic hydrogenation is inversely proportional to the value of π . This rule is found to hold for a large number of compounds. The most frequent exceptions to the rule are to be found among compounds containing the carbonyl group and among heterocyclic compounds containing nitrogen in the ring. He finds the order for the four elements to be the same as that of the ease of replacement of a given element from its compound with nickel by a different element in combination with hydrogen. "The readiness with which an atomic group is separated during the catalytic hydrogenation of a compound is greater, the greater its affinity to the catalyst; it is the smaller, the greater is its affinity to the remainder of the molecule. For this reason, the stability of a given linkage in the absence of a catalyst need not be the same as in its presence."

H. S. Taylor and Lavin¹ have attempted to determine the nature of the influence of specific surface on chain reactions involved in the oxygen-hydrogen system. In this they have assumed that hydrogen atoms, oxygen atoms, and hydroxyl radicals are the only atoms or radicals involved in the chain. Their results show that the nature of the surface is of fundamental importance in determining the velocity of atom-radical reactions. Potassium chloride is more efficient than clean glass in the H-OH combination. Alumina is also very efficient for the same reaction. Both, however, are inefficient catalysts in the recombination of hydrogen atoms. "Potassium hydroxide and carbonate, and especially, zinc-chromium oxide, are efficient agents for this reaction, as are also metallic surfaces." They have shown quite conclusively that a dehydrating catalyst, like alumina, promotes the H-OH combination, while the dehydrogenating catalyst, zinc-chromium oxide, promotes the H-H recombination.

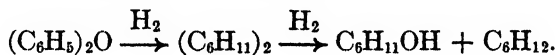
Fine foam produced by forcing air through porous bodies into water containing a foam-producing substance, like saponin, has been successfully used in extinguishing highly combustible liquids. The relatively large volume of air which can be added to the burning hydrocarbon does not support the combustion of the burning gases, but it does take part in extinguishing the combustion already begun. Strange as it may seem, foam particles containing detonating gas or oxygen-acetylene mixtures do not explode when brought in contact with a flame or with the spark of an induction coil.² Burning benzine can be as easily extinguished by a detonating gas foam as by one containing carbon dioxide. It may be said in explanation of the behavior of explosive gas foams that not only does the highly developed liquid film influence to a high degree the behavior of the gas within, but it also hinders the propagation of the combustion. Conversely, these highly developed liquid films containing the proper catalyst enhance greatly the reactivity of gases. Biesalski finds that a colloidal solution of palladium containing 1/10 percent of saponin increases

¹ H. S. Taylor and Lavin: *J. Am. Chem. Soc.*, **52**, 1910 (1930).

² Biesalski, Kowalski and Wacker: *Ber.*, **63B**, 1698 (1930); Biesalski: *Z. angew. Chem.*, **41**, 853 (1928).

enormously the speed of hydrogenation of ethylene, acetylene and salts of unsaturated fatty acids. It is essential that the foam-producing substance produce small stable homogeneous bubbles of high capillary activity. Through the use of fine bubbles the adsorptive power of the hydrogenating agent is increased two to three times that required by the laws of Gibbs.

Diphenyl ether in contact with nickel at 250° is reduced by hydrogen under 60 atms. to cyclohexane.¹ At 170° the products are cyclohexane, cyclohexanol, and traces of dicyclohexylester. Benzene, cyclohexane, phenol and cyclohexanol follow from the decomposition at 220°. Two possible explanations have been put forth for the mechanism of the reaction. The first involves the initial disruption of the carbon-oxygen linkage, followed by the hydrogenation of the benzene nucleus of the molecules decomposed. This view is favored by the isolation from the reaction product of benzene and phenol, along with their reduction products. The occurrence of benzene in abundance is ascribed to the difficulty of its hydrogenation, whereas phenol is easily hydrogenated. A second explanation of the formation of cyclohexane and cyclohexanol is given by the reaction



That is, since some benzene is obtained, they believe that the hydrogenation may occur after the ether has been split, rather than before.

Komatsu and Masumoto² find also that furfural with nickel and hydrogen at 160° and 100 atms. gives furane, methyl furane and furfuryl alcohol. Tetrahydrofurfuryl alcohol is obtained at 180° and 85 atms. Dihydrofurfuryl alcohol is formed by partial hydrogenation at 144° and 80 atms. Furfural is completely hydrogenated by heating at 150° and 100 atms. A depression of the pressure at a number of temperatures is taken to indicate that the hydrogenation proceeds in steps, depending on the temperature to which the reacting system is subjected. Tetrahydrofurfuryl ether is assumed to occur as an intermediate reaction product. This is transformed by heat to methylfurane, furane and n-butyl alcohol by disruption of the carbon-oxygen linkage.

The hydrogenation of acetoacetic ester over a nickel catalyst takes place readily³ at 100° to 150°. The rate of reduction is about three times as fast in ether or methylcyclohexane as in the absence of a solvent. The rate of reduction in ethanol is intermediate between that of the pure ester and its solution in cyclohexanol, ethyl-β-hydroxy butyrate being formed practically quantitatively. The dehydroacetic acid, formed in small quantities in the reduction of the acetoacetic ester, is reduced in methylcyclohexanol at 185° to 190° under 108 to 305 atms., the reduction proceeding about four times more rapidly at the highest than at the lowest pressure. The chief product in the hydrogenation of dehydroacetic acid is 4-heptanone.

¹ Komatsu and Masumoto: Bull. Chem. Soc. Japan, 5, 241 (1930).

² Loc. cit.

³ Adkins, Connor and Cramer: J. Am. Chem. Soc., 52, 5192 (1930).

Nitrobenzene with hydrogen in the presence of reduced nickel at 100° and 50 atms. gives aniline. At 200° and 100 atms. the main product is cyclohexamine with small amounts of dicyclohexylamine and aniline. Aniline itself gives a similar mixture at 180° and 150 atms. Nitrophenols and nitronaphthalenes show similar transformations at high temperatures and high pressures.

In alcoholic solution, 2-4-dinitrophenol is reduced¹ to the diaminophenol in the presence of nickel and hydrogen under 500 pounds pressure. Maximum yields are obtained at 96°. Elevation of temperature produces a slight decrease in the yield of amine due to the formation of ammonia. A maximum yield of 91.5 percent is obtained with a concentration of 5 g. of nitrophenol to 20 cc. of alcohol, the yield decreasing with both higher and lower concentrations. An increase in the ratio, (g. catalyst)/(g. dinitrophenol), from 0.2 to 0.4 produces an increase in the diamine yield at all concentrations.

When heated with hydrogen at 80 atms. over copper at 200° to 230° benzene is hydrogenated to a product containing 15 per cent of cyclohexane. Under the same conditions, but at 200°, naphthalene is transformed quantitatively to tetrahydronaphthalene, and this in turn at 260° passes partially to dekalin. Under practically similar conditions phenol is changed to cyclohexane and a trace of diphenyl ether; the α - and β -naphthols are hydrogenated to the tetrahydronaphthols.

It has been found by Brown and his co-workers that the hydrogenating activity of lead, thallium, bismuth, and the lower oxides of iron, tin, molybdenum and vanadium give high yields of aniline from nitrobenzene. Under the proper working conditions, thallium and bismuth also give very good yields of azobenzene. Hartman and Brown² have recently studied the hydrogenating activity of cadmium from the reduced oxalate and hydroxide. At low temperatures slightly higher yields of aniline are obtained over the reduced oxalate; the reverse is true at higher temperatures. Both catalysts give maximum yields at 319°. Previous roasting of the catalyst before reduction seems to produce a more finely divided catalyst and thus increase its activity. Cadmium still retains its activity above its melting point so long as the nitrobenzene is continually passed through the catalyst. In the absence of the nitrobenzene there is a tendency for the cadmium droplets to coalesce. Although support materials, like pumice and asbestos, do not improve the aniline yields, they do prolong the activity of the catalyst by retarding the coalescence of the cadmium droplets near the melting point.

Hill and Kistiakowski³ find that hydrogen and ethylene react when brought in contact with distilled cesium at 25°. The reaction proceeds much more rapidly at 200°. The rate of reaction at both temperatures, as indicated by the pressure drop, shows evidence of poisoning. A similar poisoning is observed in the reaction between carbon monoxide and hydrogen at room temperature. This reaction also begins very rapidly and then as rapidly diminishes

¹ Bradt: *J. Phys. Chem.*, **34**, 2711 (1930).

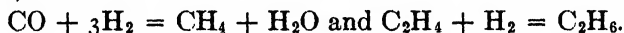
² Hartman and Brown: *J. Phys. Chem.*, **34**, 2651 (1930).

³ Hill and Kistiakowski: *J. Am. Chem. Soc.*, **52**, 892 (1930).

to zero. The reaction products of the first reaction contain ethane and cesium hydride, deposited as a white layer upon the cesium surface. While the mutual reactivity of the hydride and ethylene is very slight at room temperature, the reaction becomes quite rapid at 200° , and the hydride is removed. The resulting gases contain ethane and hydrogen, the latter being formed by the thermal decomposition of the hydride. Ethylene also poisons the surface of the cesium.

While hydrogenations catalyzed by alkali metals might appear to be explainable on the basis of the formation of intermediate compounds, the experiments of Hill and Kistiakowski seem to show that even over alkali metals only the adsorbed hydrogen is available for hydrogenation. Hydride formation serves only in diminishing the extent of free surface. Pease and Stewart¹ have previously shown also that while calcium hydride is an efficient catalyst for the reaction, the hydrogenation of ethylene over calcium does not proceed through the formation of the intermediate hydride.

Reduced rhenium and rhenium-copper catalysts catalytically hydrogenate the reactions;



While the copper-free rhenium quickly loses its activity, it may again be regenerated by heating with hydrogen at 400° .² In the reduction of carbon monoxide rhenium possesses about the same activity as osmium. A 50 percent volume contraction is obtained when carbon monoxide is led over a rhenium-copper catalyst at 470° , indicating a quantitative decomposition of carbon monoxide to carbon and carbon dioxide. After a short time the reaction ceases completely. Externally the catalyst showed no change, but yielded 41 cc. of carbon dioxide on treatment with oxygen. The reaction proceeds only to the formation of a rhenium carbide, which, like the carbides of iron and nickel, does not catalyze the decomposition of carbon monoxide. After heating with air it is again capable of carbide formation.

With platinum oxide as catalyst, isoquinoline in acetic acid solution is readily hydrogenated to tetrahydroisoquinoline at room temperature.³

It has been more or less of a common belief that the sulfur in proteins would poison noble metal catalysts. For this reason no attempt has been made to catalytically hydrogenate the proteins. Bergmann and Michalis⁴ have found that cystine, dialanylecystine and di- β -amino-ethyl sulfide are readily hydrogenated and almost quantitatively to the corresponding thiol compounds by palladium sponge in hydrochloric solution. Platinum catalysts, however, cannot be used for these hydrogenations.

Tetrahydrocarbazol in benzene is easily dehydrogenated by safrole to carbazole in the presence of palladium black.⁵ Hydrocoumarin in anethol when heated with palladium gives a small amount of coumarin. Safrole does

¹ Pease and Stewart: *J. Am. Chem. Soc.*, **47**, 2763 (1925).

² Tropsch and Kassler: *Ber.*, **53B**, 2149 (1930).

³ Ranedo and Vidal: *Anal. Fis. Quim.*, **28**, 76 (1930).

⁴ Bergmann and Michalis: *Ber.*, **53B**, 987 (1930).

⁵ Akabori and Saito: *Proc. Imp. Acad. Japan*, **6**, 236 (1930).

not reduce hydrohydrastinine in benzene when boiled with palladium, but dihydrohydrastinium salts are formed when treated with two mols of maleic acid in aqueous solution. Tetrahydroharman and tetrahydroharmine are dehydrogenated to harman and harmine, respectively, by heating with maleic acid and palladium.

Levulinic acid is easily reduced¹ to n-valerolactone in the presence of platinum oxide at room temperature. The speed of the reduction depends upon the solvent used. It is approximately 3.5 times faster in diethyl ether than in ethyl alcohol, and 4.5 times faster than in glacial acetic acid.

Conant and Hyde² find that the reduction of magnesium-free chlorophyll derivatives by the action of hydrogen and a palladium catalyst in alkaline solution does not lead to the formation of leuco compounds. They state that the reductions produced by hydrogen in the presence of palladized asbestos are not catalytic hydrogenations, but are reduction processes occurring at the potential level of the hydrogen electrode. They cite also in this connection the inability of palladized asbestos to add hydrogen to such double bonds as those which occur in allyl alcohol or in dimethylacrylic acid. The chlorophyll derivatives and the porphyrins, however, are easily hydrogenated catalytically to the leuco compounds in the presence of platinum oxide catalysts.

Coals containing no mineral constituents give only negligible quantities of oil on hydrogenation.³ Of all the mineral constituents of coal only the iron compounds are of importance as hydrogenating catalysts, and of these FeS_2 is probably the best. Added Fe_2O_3 catalytically influences the hydrogenation and produces better oil yields, especially with older coals. Its catalytic influence on younger coals is less, and in general, these require more Fe_2O_3 . Zinc chloride is still more active than the iron oxide and is good for coals of higher carbon content.

Dehydrogenation

Although the reaction products, hydrogen and naphthalene, exert no influence upon the speed of dehydrogenation of decahydronaphthalene in the presence of osmium, the products formed in the subsequent catalytic decomposition of naphthalene are poisonous to osmium.⁴ Thus, osmium is not a suitable catalyst for this dehydrogenation. Its catalytic activity may be restored, however, by heating with hydrogen at 270° . With osmium the activation energy of dehydrogenation is 10,000 cal. per mol. In this respect the metal resembles nickel, on which the heat of activation of the decahydronaphthalene is 9,990 cal. per mol. After the catalyst had been used for some time its activity was abruptly increased and the heat of activation rose to 16,250 cal. per mol, a value about the same as that observed with palladium. Balandin attempts to explain this sharp increase in the activity of osmium on the basis of his "Multiplet Theory," according to which a catalytically active center is composed of several atoms of the catalyst substance. The sudden

¹ Schutte and Thomas: J. Am. Chem. Soc., 52, 3010 (1930).

² Conant and Hyde: J. Am. Chem. Soc., 52, 1233 (1930).

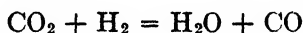
³ Hlavica: Brennstoff Chem., 10, 201 (1930).

⁴ Balandin: Z. physik. Chem., B 9, 49 (1930).

change is then associated with a regrouping, or displacement of the metal atoms in the catalyst surface, whereby both the formation, as well as the adsorption of the poisonous substances is decreased, and thus the dehydrogenation catalysis of the decahydronaphthalene is favored. The failure of osmium to dehydrogenate other six membered ring systems is explained as probably due to the more rapid formation of the inhibiting substances.

Kodama¹ has studied the influence of added metallic oxides upon the copper-cobalt catalyst used in the reduction of carbon monoxide. MgO proved to be the most efficient promoter; it becomes active at 200°, but gives the best results at 240°. It was still sufficiently active after 16 hours use to bring about a 45 percent gas contraction. Petroleum and benzene are found among the products. With additions of TiO₂, ZrO₂ or CeO₂ liquid products are first obtained at 180°-200°. The gas contractions are about the same for the three promoters at the same temperature. All three catalyze the formation of hydrocarbon gases, and to a slight extent some liquid products. While ZrO₂ is the best promoter of the three, it is still not so good as MgO. Beryllium and zinc oxides are of little use as promoters, and cadmium oxide completely inhibits the activity of the cobalt.

Attempts to reduce carbon dioxide according to the reaction,



have, heretofore, been carried out only at relatively high temperatures. The same reaction has been found to take place at moderate temperatures when the proper catalysts are employed.² With metallic copper the reaction is noticeable at 200°. Employment of Cu-Cr₂O₃, Fe-Cu, Fe-Co and Cu-Co-Zn contacts at temperatures between 200° and 450° and with mixtures of carbon dioxide and hydrogen in the ratio of 1:1 and 1:3, respectively, give yields of carbon monoxide up to 16 percent. With long contact, and especially with contacts containing cobalt, there is complete reduction of carbon monoxide to methane.

Molybdenum sulfide, MoS₃ is most efficient catalyst in the high pressure reduction of cresols at 460°-80° and pressures up to 240 kg./sq. cm. It gives a nearly complete reduction to hydrocarbons. While nickel, or its hydroxide, are good catalysts their efficiency is strongly influenced by the presence of sulfur. The phenols are reduced by a hydrogenation of the hydrocarbons formed more with nickel than with molybdenum catalysts. No cyclic alcohols are formed. Of the large number of catalysts employed ZnCl₂, Al(OH)₃, (NH₄)₃VO₄, Cr(OH)₃, UO₃, Co(OH)₂ and NiS were excellent catalysts; ZnO, basic copper chromate, WO₃ and Fe(OH)₃ are inactive.

Oxidation

In 1910 J. J. Thomson³ called attention to the fact that combustion involves not only the molecules and the atoms, but also the electrons. He

¹ Kodama: *Sci. Papers Inst. Phys. Chem. Res.*, **13**, 93; **14**, 13 (1930).

² Bahr: *Ges. Abhandl. Kenntniss Kohle*, **8**, 219 (1930).

³ J. J. Thomson: *Brit. Ass. Rep.*, Sheffield, 1910, 501.

stated that it was not improbable that the emission of charged particles from a surface is of primary importance in promoting combustion on hot surfaces. That these electrons might produce very important effects by union with oxygen, with moisture, or with the combustible material. Finally, that the action of surfaces might ultimately be found to depend on the fact that they form a support for layers of electrified gas in which chemical changes proceed with high velocity.

While the emission of electrons from tungsten is not affected by chemically indifferent gases, it is suppressed by the catalytic poisons.¹ The photoelectric emission from metals is also decreased by the catalytic poisons, HCN, H₂S and CO.² Thomson has also found that thermionic emission becomes perceptible when heated to the temperature at which it catalyzes the union of hydrogen and oxygen.³ While variation of the proportion of hydrogen in the mixture does not alter the temperature at which the union takes place, an excess of oxygen does reduce the temperature of the combination below that of thermionic emission. Thus, oxygen becomes active toward hydrogen at a platinum surface at a temperature lower than that at which electrons are emitted from the surface. The activation of hydrogen occurs at the same temperatures as that at which thermionic emission becomes perceptible. Srikantan⁴ has extended the experiments of Thomson to the study of reactions between hydrogen and carbon dioxide at the surfaces of filaments of platinum, of platinum coated with barium oxide, and of thoriated tungsten. The adsorptive capacity for carbon dioxide is greatly increased by using the coated platinum. The thoriated tungsten emits electrons with great ease at temperatures far below that required for dull red heat. Does the reaction between these two gases take place at the temperature at which thermionic emission becomes perceptible as in the case of platinum? It was found that while increase of hydrogen or carbon dioxide does not alter the temperature at which the reaction begins on the coated platinum, the temperature is far lower than that on the surface of plane platinum. The catalytic reaction on the thoriated tungsten begins at the temperature at which thermionic emission is just perceptible. These experiments clearly indicate that the activation of the gases on a catalyst surface is influenced to a large extent by the capacity of the surface to emit electrons at the temperature employed.

Thomson⁵ has studied the condition of explosions of stoichiometric mixtures of carbon disulfide and oxygen. He finds that the reaction is very slow below 140°. It proceeds explosively, however, at a few degrees above 140°, if the pressure lies within certain limits. The transition from a slow reaction to an explosive combustion is sharp at the limiting pressures. Elevation of temperature widens the pressure limits within which explosion occurs. Upon crossing heated carbon disulfide and oxygen rays in the wall-free space the

¹ Langmuir: *Trans. Faraday Soc.*, **17**, 641 (1929).

² Kruger and Taege: *Z. Elektrochemie*, **21**, 562 (1915).

³ Thomson: *Physik. Z.*, **14**, 11 (1913).

⁴ Srikantan: *Indian J. Physics*, **5**, 685 (1930).

⁵ Thomson: *Z. physik. Chem.*, **B 10**, 273 (1930).

explosion was first observed at about 290° . It occurred at a much lower temperature when the rays were allowed to impinge upon a glass rod. These relations are not in agreement with the views of Alyea and Haber.¹ According to these authors, the upper pressure limit is the limit of ignition at the walls; the lower pressure limit is the limit of propagation of ignition through the free space. The chain reaction manifested in the combustion of carbon disulfide is analogous to that observed in the ignition of oxy-hydrogen gas at low pressures. In both cases the explosion begins at the wall.

The much greater influence of hydrocarbon concentration than of oxygen concentration on the rate of oxidation of ethylene and benzene has been found² to apply also to the oxidation of methane, methyl alcohol and acetaldehyde. While all of the reactions proceed by chains, the length of the chain and the methods by which it is ended vary considerably from reaction to reaction. With benzene the chains do not appear to reach the wall unless the free space of the reaction vessel is very small, while with methyl alcohol nearly all of the chains appear to end at the wall. The actual qualitative nature and condition of the wall, the extent of surface and dimensions of the vessel are found to exert a considerable influence upon the reaction rate. The variability of the nature of the wall and its ability to end a chain is assumed as due to variations in the adsorbed gas layers, and here in particular to adsorbed oxygen. If the reaction chains begin in the gas phase and end at the wall, the reaction will be much slower in a vessel of small than in one of large size. But, if the chains end for the most part in the gas phase, the dimensions of the vessel are unimportant. All three of the reactions studied were found by Fort and Hinshelwood to be slowed down considerably by a sufficient increase in wall surface. Thus, for example, with methane the reaction did not proceed at all in 30 minutes in a vessel filled with silica spheres. To explain their results with methyl alcohol they assumed that the efficiency of the walls in ending the chains depends upon the layer of adsorbed oxygen.

The mechanism of the oxidation of metals has been the subject of frequent investigations. Tammann and his co-workers,³ and also Vernon⁴ have studied the oxidation of copper at low temperatures. At high temperatures we have the comprehensive work of Pilling and Bedworth⁵ and of Dunn.⁶ While the results of all of these investigators lead to the conclusion that the speed of oxidation is conditioned by the speed with which the oxygen diffuses through the oxide layer formed, there is some disagreement as to the laws under which the diffusion takes place.

Pilling and Bedworth have shown that in so far as the kinetics of oxidation is concerned, metals may be divided into two classes, depending upon

¹ Alyea and Haber: *Naturwissenschaften*, 1930, 441.

² Fort and Hinshelwood: *Proc. Roy. Soc.*, 129A, 284 (1930).

³ Tammann: *Z. anorg. allgem. Chem.*, 123, 197 (1923); 128, 179 (1923); 152, 149 (1926); 169, 43 (1927).

⁴ Vernon: *J. Chem. Soc.*, 1926, 2273.

⁵ Pilling and Bedworth: *J. Inst. Metals*, 29, 529 (1923).

⁶ Dunn: *Proc. Roy. Soc.*, 111A, 211 (1926).

whether the volume of the oxide is greater or less than that of the metal from which it is formed. If greater, the oxide formed will protect the remaining metal from oxidation; if the volume of the oxide is smaller, its porous nature can offer no protection to the metal below. Copper belongs to the first group. They have shown that when the oxide covers the metal completely the rate of oxidation is governed completely by the rate of diffusion of the oxygen through the oxide. Assuming the rate of diffusion of the oxygen to be inversely proportional to the thickness of the oxide layer, we may write

$$dx/dt = k/x. \quad (1)$$

This upon integration becomes

$$x^2 = k \cdot t, \quad (2)$$

where x is the weight of the oxide formed in time t and k is a constant. This equation was found to accurately describe the rate of oxidation of metals of the first group with the exception of copper.

Dunn¹ finds that the oxidation of commercial copper follows (2) over short intervals of time. However, if the copper has been previously activated by alternate oxidation and reduction, this law is not obeyed even for the shortest time intervals. In discussing the nature of the diffusion of oxygen through the oxide Dunn assumes that, (1) "the structural units of the oxide are in a state of vibration and that a random distribution of energies of vibration prevails; (2) that an oxygen molecule can only pass a structural unit, if this possesses at the moment energy greater than the critical energy, causing a loosening of the oxide at that point."

Whether or not oxygen can diffuse through the Cu_2O lattice will naturally depend upon the relative dimensions of the oxygen and the lattice. Taking the edge of the cubic cell² of Cu_2O as 4.28\AA and the diameter of the oxygen ion³ as 2.7\AA , and neglecting the size of the copper ion, Wilkins and Rideal⁴ have shown that there is not sufficient room for the oxygen molecule of diameter⁵ 3.62\AA to pass through a stable lattice. While this may be true for low temperatures, the diffusion should be facilitated at high temperatures where the lattice is much less stable. Experimental evidence obtained at temperatures around 1000° , near the melting point of copper (1235°), appeared to support these considerations.

Wilkins and Rideal⁶ claim that the rate of oxidation of copper must be dependent upon the rates of at least three processes: (a) condensation of oxygen at the $\text{Cu}_2\text{O}-\text{O}_2$ interface; (b) evaporation of the oxygen from this oxide-oxygen interface into the body of the oxide; and (c) the diffusion of oxygen through the oxide. They find at constant temperature that the low pressure oxidation of activated copper follows the simple relation:

¹ Dunn: Proc. Roy. Soc., 111A, 219 (1926).

² Greenwood: Phil. Mag., 48, 653 (1924).

³ Bragg and West: Proc. Roy. Soc., 114A, 45 (1927).

⁴ Wilkins and Rideal: Proc. Roy. Soc., 128A, 394 (1930).

⁵ Jeans: "Dynamical Theory of Gases," 327.

⁶ Loc. cit.

$$\log p_0/p = kt, \quad (3)$$

where p_0 is the initial pressure of the oxygen, p is the pressure at the time t , and k is a constant. Relation (3) fails completely, however, when applied either to the oxidation of activated copper at high pressures, or to the oxidation of inactive copper at low pressures.

Feitknecht¹ finds that the speed of oxidation of copper at high temperatures does not exactly follow the parabolic law, $x^2 = K \cdot t$. Initially, the speed is too great and only after an initial oxidation of a few minutes is the validity of the law fulfilled. The oxide layer at all temperatures consists chiefly of Cu_2O , covered superficially by a thin film of CuO . The Cu_2O layer has a metallic-like structure, it shows crystal growth, and thus exhibits the same regularities as metals. According to Feitknecht, it is these observations on the crystal growth of Cu_2O that gives us a possible explanation for the deviations of the experimental results from the regularities demanded by theory. The diffusion of the oxygen takes place both through the lattice structure of the Cu_2O crystals and along their boundary edges. Since the extent of the crystal surface varies inversely with the square of the size of the crystallites, the proportion of oxygen diffusing along the boundary surfaces will increase strongly with decrease in the size of the crystals. Hence, if the Cu_2O layer is thin and the crystallite is small, the speed of oxidation is initially greater than that corresponding to the parabolic equation. Later, when the crystals become larger and cover the surface, almost all of the diffusion is through the crystal lattice and the law is obeyed.

Wilkins² takes issue with Feitknecht, and he maintains that the latter's conclusions deduced from experimental results are not justifiable for the following reasons. He states that equation (2) above is derived from (1), a relation which implies that the rate of oxidation is controlled by the speed of diffusion of oxygen through the Cu_2O layer. He claims that (2) follows from (1) only if the integration constant is zero. This can only be the case, however, if no oxidation has taken place up to the time from which measurements were made. For these reasons Wilkins advocates the use of the more general parabolic law:

$$X^2 = k \cdot t + c, \quad (4)$$

where \sqrt{c} represents the amount of preoxidation. This more general equation is found to be in agreement with Feitknecht's own data. Wilkins states that we must assume that the permeability of the oxide layer remains unchanged during oxidation. Also, that the diffusion occurring at the boundary of crystals plays only a slight rôle in the transfer of oxygen through the $\text{Cu-Cu}_2\text{O}$ interface. Its contribution at high temperatures is small compared with lattice diffusion. In a study of the influence of pressure Wilkins³ finds that the oxidation of copper obeys the relation: $d(p_0 - p)/dt = k(p_0 - p)$, down to pressures of about 10 mm. Activation of the copper increases the

¹ Feitknecht: *Z. Elektrochemie*, **35**, 142 (1929); **36**, 16 (1930).

² Wilkins: *Z. Elektrochemie*, **35**, 500 (1929).

³ Wilkins: *Proc. Roy. Soc.*, **128A**, 407 (1930).

limiting pressure, that is, the pressure below which the oxidation ceases to be independent of the oxygen pressure, thirteen times, while sintering the surface increases it. He suggests that at the limiting pressure the grain boundaries of the Cu_2O crystals are just saturated with oxygen, and that the adsorbed gas diffuses laterally at 183° . At this temperature the parabolic law holds for long periods, provided that the copper is activated and the oxygen pressure is sufficiently high.

Lewis¹ finds that glass and pumice raise the ignition temperature of the hydrocarbons, the amount depending on the rate of heating and the concentration. Charcoal, however, raises the ignition temperature of the paraffins and lowers that of the olefins, the amount in each case varying with the nature of the charcoal. The effect of metals on the ignition point varies with the metal employed, with the extent and condition of the surface, with the concentration of the hydrocarbon, and with the speed of heating. They may raise the temperature or may have no effect at all; in some cases they may even prevent explosion. Thus, silver and platinum increase considerably the ignition temperatures; tin, zinc and aluminum show practically no effect. Lead raises the ignition temperature considerably and may even inhibit explosions. Copper also prevents the ignition of some hydrocarbons. The effect of the last two metals decreases as the molecular weight of the hydrocarbons becomes smaller.

Lewis suggests a three-stage mechanism for the combustion of paraffin hydrocarbons: (1) a primary dehydrogenation yielding unsaturated hydrocarbons, (2) the combination of these with oxygen to give unstable peroxides, and (3) the decomposition of these to aldehydes, etc., which are then oxidized to water and the oxides of carbon.

In the Haber-Bosch process water gas containing nitrogen, mixed with three to four volumes of steam, is passed over promoted iron catalysts. After scrubbing to remove the CO and CO_2 the effluent gas gives a 3 to 1 hydrogen-nitrogen mixture suitable for the synthesis of ammonia. Attempts to remove the residual CO from the hydrogen by preferential oxidation have met with considerable success provided the CO concentration does not exceed 0.5 percent. Lamb, Scalione and Edgar² have shown the possibility of preferentially oxidizing the 0.5 percent CO in the hydrogen by adding an amount of oxygen in excess of that required for complete oxidation of the carbon monoxide, then saturating with water vapor at 40° and passing it over hopcalite in small-bore copper tubes immersed in liquid baths. Water vapor poisons³ the hopcalite toward the oxidation of both the carbon monoxide and the hydrogen, but more especially toward the latter. Lamb and Vail find that the water vapor concentration in the gas phase may be greatly increased since, as they found, the activity of the hopcalite depends not upon the concentration of the water in the gas phase, but upon the water content of the catalyst. Further, the activity is practically independent of the temperature.

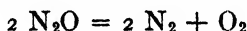
¹ Lewis: *J. Chem. Soc.*, 1930, 34, 58.

² Lamb, Scalione and Edgar: *J. Am. Chem. Soc.*, 44, 738 (1922).

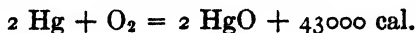
³ Lamb and Vail: *J. Am. Chem. Soc.*, 47, 123 (1925).

Believing that the use of a large excess of steam in the gas phase and high temperatures should be efficacious in the oxidation of carbon monoxide, Keuntzel¹ passed water gas containing a large excess of steam over catalysts of CuO, MnO₂, and two hopcalite mixtures. The two oxides and a 5-component hopcalite were catalytically active but all three suffered reduction and loss of catalytic activity. Only the 2-component hopcalite (MnO₂ 60: CuO 40) gave promise of preferential oxidation under the operating conditions employed. It gave a 96 percent efficiency for 37 hours. With a water gas of the initial composition: 1.3 CO, 1.5 O₂, 49.5 H₂, 28 CO₂ and 19.7 N₂ plus three volumes of water vapor over a commercial hopcalite 97 to 99 percent of the CO was oxidized to CO₂ in the temperature range of 160° to 195°. A "CWS" hopcalite in a copper chamber with the same mixture gave a 100 percent oxidation for several hours, then gradually falling to 96 percent after 69 hours of service. The loss of catalytic efficiency is apparently due to the reduction of the oxide by hydrogen and carbon monoxide, the loss of available oxygen through thermal decomposition of the oxides and to inefficient dissipation of heat. The steam serves to rapidly dissipate the heat of the reaction, preventing local overheating of the catalyst granules. It specifically inhibits the reduction of the catalyst and the oxidation of the hydrogen.

In the investigation of the decomposition of nitrous oxide on platinum at low pressures, Schmieschek² found evidence for an interesting low-pressure oxidation. The increase in pressure in the presence of platinum is less than we should expect if the oxide is to decompose according to the reaction:



He explains this anomalous pressure effect as due to the disappearance of oxygen brought about by the formation of mercuric oxide. Independently, Leipunski³ has studied the speed of oxidation of mercury in its dependence upon the partial pressure of the oxygen and mercury vapor in the presence of glowing platinum. He finds that the reaction speed is independent of the oxygen pressure and that it decreases with increasing mercury vapor pressure. Without a catalyst mercury combines with oxygen of atmospheric pressure at 300° to form the oxide:



This reaction is reversible and, as we know, the oxide begins to decompose at 400°. Leipunski finds, however, that mercuric oxide is formed in contact with platinum when heated above 1300°. The evidence for this lies in the fact that mercuric oxide evaporates from the platinum surface and is deposited as a reddish yellow precipitate on the cool walls of the glass vessel. Thus, owing to the minimal vapor pressure at the temperature of the wall, the oxide is removed practically completely from the reaction and mercuric oxide continues to be formed on the heated platinum. Hence the reaction

¹ Keuntzel: *J. Am. Chem. Soc.*, **52**, 437, 445 (1930).

² Schmieschek: *Dissertation*, Berlin, 1927.

³ Leipunski: *Z. physik. Chem.*, **B 1**, 369 (1928).

will go on with the disappearance of oxygen until the partial pressure of the oxygen in the vessel has fallen to the dissociation pressure of the oxide at the temperature of the wall, viz., about 5×10^{-19} mm. at 18° . In the presence of the catalyst, therefore, the reaction proceeds practically to completion.

Okayama¹ has attempted to find out if this decrease in pressure is due to the formation of mercuric oxide alone, or if there are other side reactions, such as the formation of ozone or of platinum oxide which may utilize part of the oxygen. He finds that on passing oxygen over heated platinum in the absence of mercury no ozone is formed. That platinum oxide is formed is shown by the gradual brownish coloration of the glass wall of the reaction vessel. Upon admitting oxygen the brown film becomes black and crystalline. The speed of formation of the platinum oxide was found to be so small in comparison with that of the mercuric oxide that its rôle in the removal of oxygen is negligible. Okayama states that while an increase in the mercury vapor pressure of 40-fold only causes an increase of 10 to 15 percent in the reaction speed, the influence of oxygen is considerable. This is directly contrary to the findings of Leipunsky. Okayama also finds that the reaction speed is independent of the pressure of the mercury vapor, but it follows the oxygen pressure according to the relation:

$$\frac{\Delta n}{\Delta z} = \frac{\sqrt{p}}{a + b\sqrt{p}},$$

where $\Delta n/\Delta z$ is the number of molecules of dissociated oxygen per sq. cm. of platinum surface.

It has been found² that the oxidation of ammonia to nitric acid is catalyzed best by those substances which emit radiation of the same wave lengths as those corresponding with the energy required for the dissociation of molecular to atomic nitrogen and oxygen. Calcium and silicon satisfy these requirements for oxygen; tin for nitrogen. A catalyst having the molecular composition 2.7 SnO₂, 2.7 CaO and 1 SiO₂ gives 81.5 to 86.2 percent of nitric acid from a seven per cent ammonia-air mixture. The efficiency of the catalyst at various temperatures is found to be closely related to the intensity of the radiation of the catalyst at the given temperature.

In so far as the reaction has distinctly begun, the catalytic oxidation of ammonia involves the disappearance of ammonia and the formation of nitric oxide and nitrogen in varying proportions, depending on experimental conditions. While the formation of intermediate labile compounds leading to nitrogen oxides or free nitrogen has always been assumed, opinions vary as to the nature of the intermediate compound. Some³ assume the intermediate compound to be nitroxyl, HNO. Others⁴ hold to the view that the oxidation of ammonia proceeds through the intermediate formation of the imid.

¹ Okayama: *Z. physik. Chem.*, B **6**, 355 (1930).

² Andadurov and Weinschenker: *Ukrain. Chem. J.*, **5**, 1 (1930); see *Brit. Chem. Abs.*, A, **1930**, 1132.

³ Andrussov: *Z. angew. Chem.*, **39**, 321 (1926); **40**, 166 (1927); **41**, 205, 262 (1928); *Ber.*, **59**, 458 (1926); **60**, 536, 2005 (1927); Bodenstein: *Z. angew. Chem.*, **40**, 174 (1927).

⁴ Raschig: *Z. angew. Chem.*, **40**, 1183 (1927); **41**, 207 (1928); Hofmann: *Ber.*, **50**, 204 (1926); **60**, 1190 (1927); **62**, 2509, 3000 (1929); Neumann and Manke: *Z. Elektrochemie*, **35**, 751 (1929).

Catalysts containing manganese have been found to be excellent catalysts for the oxidation of ammonia, since they bring about the oxidation at much lower temperatures. Employing mixed catalysts of MnO_2 and Bi_2O_3 at 300° , Nagel¹ was able to transform 90 percent of the ammonia used to nitrous oxide. He finds that catalysts capable of oxidizing ammonia at temperatures under about 500° yield nitrous oxide chiefly. Between 500° and 1000° nitric oxide and the higher oxides of nitrogen are formed, while at still higher temperatures nitrogen is the chief product. From the results obtained he assumes with Bodenstein that HNO is the intermediate compound. This decomposes at low temperatures to N_2O and water; at higher temperatures, however, it is oxidized to HNO_3 and NO . The formation of the free nitrogen is ascribed to a reaction between HNO and undecomposed ammonia.

Previous experiments² have shown that there is an upper limiting pressure above which the oxidation of phosphine proceeds with negligible slowness even in the absence of moisture, but below which explosion does occur. Working with perfectly dry gases, Dalton³ finds that with oxygen in large excess the mixture does not explode until expanded to very low pressures. The pressures at which explosion occurs become rapidly greater with increase in the proportion of phosphine until the ratio of the two gases becomes unity, where the oxygen pressure begins to change more slowly and beyond this point becomes nearly constant. No explosion occurs at any pressure when the PH_3/O_2 ratio is below 0.1. The explosion pressure is found to be independent of the tube diameter and of the nature of its walls, but it is decreased by the admission of inert gases. These facts tend to show that the upper limit is subject to conditions quite different from those prevailing at the lower limit. Dalton assumes that the reaction occurs through a simple chain mechanism in which the deactivation of the chains is brought about by three-body collisions in the gas.

Syntheses

It has been shown by Dodge⁴ that in the several attempts to calculate the free energy change involved in the synthesis of methanol all of the calculated free energy changes lead to values of $K_p = \left(\frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2} \right)$ which do not agree at all with the published experimental results. Apart from the direct experimental method of determining the methanol equilibrium, some investigators have employed the Nernst approximation formula to calculate K_p . The results obtained are in fair agreement with the results on high pressure synthesis. Because of the unsound theoretical basis and its complete failure in many well-established equilibria, however, Dodge regards the agreement obtained as entirely accidental. This indirect method involves no equilibrium measurements, but does involve a knowledge of heat content, free energy

¹ Nagel: *Z. Elektrochemie*, **36**, 754 (1930).

² Hinshelwood and Dalton: *Proc. Roy. Soc.*, **125A**, 294 (1930).

³ Dalton: *Proc. Roy. Soc.*, **123A**, 263 (1929).

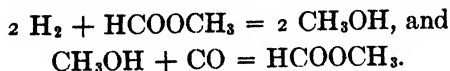
⁴ Dodge: *Ind. Eng. Chem.*, **22**, 89 (1930).

and entropy data for a series of reactions. The value of ΔF sought is the result of a difference of several much larger quantities, ΔH . A small percentage error in some of the larger values of ΔH is sufficient to make a considerable error in the calculated value of ΔF , much greater, in fact, than would the same error in the value of the absolute entropies. According to Dodge, the calculation of the free energy change for the methanol-synthesis reaction is far more dependent upon exact data for the various heats of reaction involved than upon entropy data. In support of his contention he states that an error of 0.1 percent in the heat of combustion of methanol will lead to an error of approximately 33 percent in the value of K_p for the reaction at 298.1°K.

It has been shown by Smith and Hirst¹ that carbon dioxide and hydrogen in the presence of a zinc oxide-chromium oxide catalyst at 304° react to form methanol, carbon monoxide and water. Likewise, carbon monoxide and water react to form carbon dioxide and hydrogen, and the equilibrium can be closely approached in the water gas reaction. However, owing to the fact that several reactions may occur through the action of this catalyst upon hydrogen-water-carbon dioxide mixtures at 304°, they did not find it possible to determine which reaction comes nearest to equilibrium. The suggestion is intimated that the formation of methanol from carbon monoxide and hydrogen may not be a direct process.

Wettberg and Dodge² have also studied the methanol equilibrium over a zinc chromite catalyst at 170° at 170 atmospheres and through the temperature range from 260° to 310°. A dynamic method was used and the equilibrium was approached from both sides. Their new data, however, differ considerably from results obtained by theoretical methods. The possibility of side reactions and the effect of these on the establishment of the methanol equilibrium is found to be difficult to estimate. It is obvious, so they state, that a true equilibrium cannot be established with respect to the methanol equilibrium when side reactions are proceeding simultaneously at a considerable distance from the equilibrium.

Lacy, Dunning and Storch³ have determined the equilibrium constants for the reaction $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$ by approach from both sides at 250° and 300°, and also from the synthesis side at 200°. In all experiments the pressure was 50 atms. In this they employed a supported reduced catalyst consisting of copper, uranium and thorium. The average constants, $K_p = \frac{(p_{\text{CH}_3\text{OH}})}{(p_{\text{CO}})(p_{\text{H}_2}^2)}$ at 250° and 300° are 0.00125 and 0.00010, respectively. They also calculated the equilibrium constants from measurements of equilibria in the two reactions.

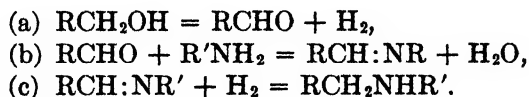


¹ Smith and Hirst: *Ind. Eng. Chem.*, **22**, 1037 (1930).

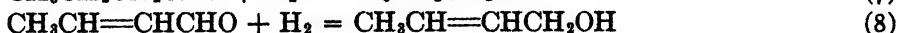
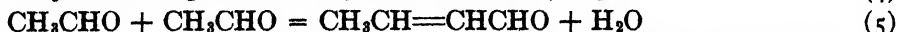
² Wettberg and Dodge: *Ind. Eng. Chem.*, **22**, 1040 (1930).

³ Lacy, Dunning and Storch: *J. Am. Chem. Soc.*, **52**, 926 (1930).

Mixtures of an alcohol and ammonia or a primary amine when passed over heated nickel, or heated with nickel under pressure at 150° to 200° give almost theoretical yields of the corresponding primary or secondary amines.¹ Cyclohexanol and ammonia at 150° give cyclohexylamine, while dicyclohexylamine is exclusively formed at 190° . Guyot and Fournier believe that the mechanism of the reaction can be represented by three successive stages, namely

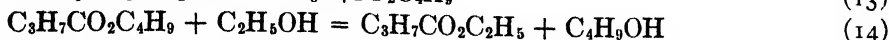
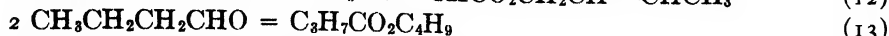
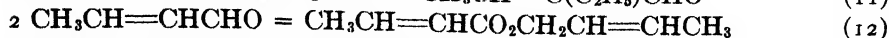
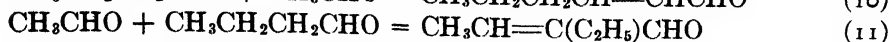


Ethanol is dehydrogenated to aldehyde when passed over zinc oxide or zinc chromite at 300° to 400° . Practically no aldehyde is produced, however, if the reaction takes place under a sufficiently high hydrogen pressure; instead of aldehyde, substances of higher molecular weight are formed. Adkins, Kinsey and Folkers² have studied the aldehyde condensation reactions over zinc chromite and zinc oxide catalysts at pressures up to 500 atmospheres. In the passage of ethanol over zinc chromite under a pressure of 500 atmospheres several products are formed; among these are liquid ethyl acetate, n-butanol and a liquid boiling above 125° , but only traces of aldehyde. Upon replacing a part of the ethanol by aldehyde they found that the condensation products obtained in a given time to be greater in amount than if the reaction were dependent upon the aldehyde produced by dehydrogenation. The products obtained under high pressures from ethanol and aldehyde over zinc chromite at 360° was so complicated a mixture that fractional separation into its components was impossible. The product was, therefore, subjected to various forms of chemical treatment. The lowest fraction from the chromite catalyst contained aldehydes, alcohols, esters and water; that from the higher fractions contained alcohols, esters, and ethers, but no appreciable amounts of aldehyde, ketones or glycols. The alcohols and esters were both saturated and unsaturated in type. The nature of the products obtained indicate the occurrence of various reactions, namely, dehydrogenation, hydrogenation, dehydration, oxidation and aldol-like condensations. A summary of the reactions through which the simpler compounds may be formed is given below.

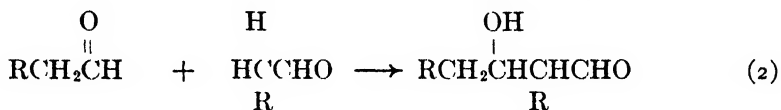
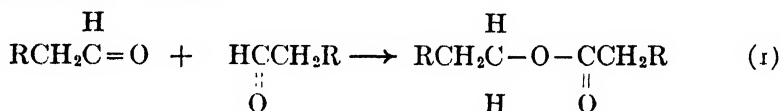


¹ Guyot and Fournier: *Compt. rend.*, **189**, 927 (1929); *Bull.*, (4) **47**, 203 (1930).

² Adkins, Kinsey and Folkers: *Ind. Eng. Chem.*, **22**, 1048 (1930).



Among these two types of reactions are to be observed. The first involves the simple dehydrogenation of an alcohol, or the reverse reaction of adding hydrogen to an aldehyde, ketone or unsaturated compound. The second type of reactions occurring on oxide catalysts are those that involve an increase in the number of carbon atoms per molecule. According to Adkins and his co-workers, it appears more than probable that the synthesis of substances of higher molecular weight from ethanol or aldehyde is dependent upon two reactions both involving the addition to each other of two molecules containing carbonyl groups—that is,



“Direct evidence is lacking that the compounds containing chains longer than two carbon atoms are dependent upon the aldol reaction (reactions 3, 5, 10, 11). However, the nature of the products is such as to make it seem reasonable that the synthesis of the higher alcohols and esters is dependent upon the reaction. Whether aldols are actually formed and then dehydrated (reactions 3 and 4) or whether the condensation takes place with the simultaneous elimination of a molecule of water and the formation of an unsaturated aldehyde (5) is questionable. In no case has any glycol been found in the distilled reaction products, which is against the first assumption. Moreover, the catalyst is not active for dehydration of alcohols. A direct reaction, as in (5), seems more reasonable.”

Manganese chromite and copper chromite behave similarly. The latter leaves almost no aldehyde in the reaction product, and produces about two and a half times as much of the esters of ethyl and butyl alcohols.

Decomposition

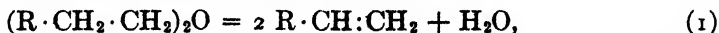
Although the equilibrium concentration of CCl_4 as calculated from its heat of formation (2543 cal.) is considerable, Bodenstein, Günther and Hoffmeister¹ were not able to synthesize it from its elements. Attempts to reach the equilibrium by the decomposition of CCl_4 showed that decompo-

¹ Bodenstein, Günther and Hoffmeister: *Z. angew. Chem.*, **39**, 875 (1926).

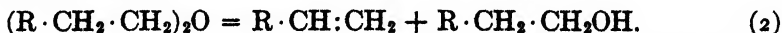
sition is possible, but the reaction stops long before the calculated equilibrium was reached. Only 4% was actually decomposed at 400°, whereas according to the Nernst approximation formula 48% should be decomposed. Bodenstein and Günther¹ have passed CCl₄ in a very slow stream over activated charcoal in a quartz tube at 400° to 500°. They find that the decomposition approximates equilibrium at high temperatures without reaching it. Their observations clearly show that the reaction stops before equilibrium is reached and this deviation is greater the lower the temperature of the decomposition. The reaction is stopped by a poisoning of the catalyst which, they explain, may be due to a superficial film of carbon from the decomposition of the CCl₄, or by the adsorption of Cl₂ and CCl₄ which diminishes with rise in temperature. It is interesting to note that the density of C from the decomposition of CCl₄ ranges from 2.3 to 2.5,² whereas the density of ordinary amorphous carbon is 1.8.

Bahr and Jessen³ find that while finely divided metallic cobalt does not decompose CO at 225°, the dissociation does take place on cobalt containing 9.24 percent of Co₂C. At temperatures above 225° the carbide gives free carbon. No carbide prepared from the dissociation of carbon monoxide on finely divided cobalt was found to give up its carbide carbon on treatment with hydrogen at temperatures as low as 240° to 250°. However, carbide formed from the free elements does form methane on heating with hydrogen above 400°.

In recent years the chemists of Japan have made extended applications of the use of a Japanese acid clay in many catalytic processes. Kashima⁴ has studied the decomposition of ethyl, n-propyl, n-butyl, n-amyl and ethyl-n-butyl ethers over activated Japanese clay at temperatures between 200° and 400°. The chief decomposition products of the ethers are olefins, alcohols and water. There is formed also small amounts of aldehyde, gaseous products (CO₂, CO, O₂, H₂), and sometimes ester and a species of a petroleum hydrocarbon. A very slight amount of carbon is deposited upon the catalyst. That olefins and water are formed by the reaction:



is confirmed by the fact that at temperatures above 300° the ratios of olefin to water are almost constant (2:1). Further, the yields of olefins from ethers are always greater than those from the corresponding alcohols. Kashima assumes that the alcohols produced in the decomposition of ethers may very probably arise through the reaction:



The decomposition of ethyl-butyl ether gives rise to a mixture of ethylene, butylene, ethanol, butanol and water. Since the amounts of butylene and ethanol are larger than those of ethylene and butanol, the affinity between

¹ Bodenstein and Günther: *Z. angew. Chem.*, **43**, 423 (1930).

² Tammann: *Z. angew. Chem.*, **115**, 145 (1921).

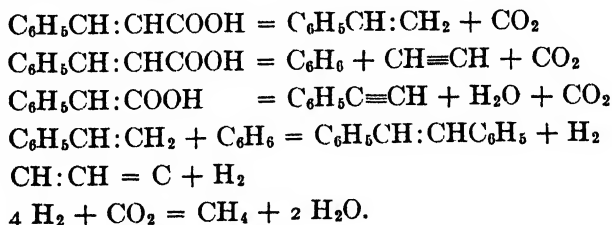
³ Bahr and Jessen: *Ber.*, **63B**, 2226 (1930).

⁴ Kashima: *Bull. Chem. Soc. Japan*, **5**, 25 (1930).

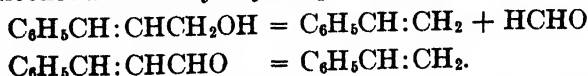
the butyl group and oxygen must be less than that between the ethylene group and oxygen. At low temperatures (200° - 250°) the ethers yield the corresponding alcohols, the amount of alcohol decreasing with rise in temperature. The ethylene yield, on the contrary, increases with rise in temperature and practically dominates the reaction above 300° . In general, the double bond of the olefin is formed on the carbon atom previously attached to the oxygen. With butyl ether, however, the butylene produced is found to be a mixture of the α and β isomers, with the latter in excess. The migration of the double bond through the action of the clay leads to the formation of the most stable isomer.

Ethylene, acetylene, propylene and trimethylene are unstable in the presence of copper or nickel at 200° . Acetylene spontaneously decomposes under these conditions, depositing carbon and forming various aromatic products and cuprene.¹ Mixtures of naphthalene with ethylene or acetylene, and of benzene with either of these two gases show no decomposition in the presence of nickel at 200° . The stability of the ethylene and the acetylene appeared to be due to dilution with benzene or naphthalene. When however, phenylethylene was passed over nickel, not the slightest decomposition was observed at 350° , it became apparent that the stability of the unsaturated linkages might be attributed to the influence of contiguous groups.

Goswana² has attempted to determine the influence of the contiguous groups attached to unsaturated linkages when the vapors of the compounds are passed over nickel at 350° . Phenyl-acetylene, sym-diphenylethylene and ethyl cinnamate do not decompose. Eugenol is only partially transformed to isoeugenol. While ethyl cinnamate, with its $\text{CH}=\text{CH}$ group attached to the phenyl and carbethoxy radicals, does not suffer decomposition, the case is very different with cinnamic acid, alcohol and aldehyde. Cinnamic acid decomposes in several steps:



At 350° the alcohol and aldehyde yield phenylethylene:



Their results show that the phenyl and the carbethoxy groups have a stabilizing influence on unsaturated linkages. Whereas the COOH , CHO and CH_2OH groups do not protect the unsaturated portions. It is interesting to note in this respect that the enolic ethyl-acetoacetate decomposes to acetone,

¹ Sabatier and Senderens: Bull., 21, 530 (1899); Compt. rend., 130, 250 (1900); 134, 1127 (1902).

² Goswana: J. Indian Chem. Soc., 7, 647 (1930).

carbon dioxide and ethylene. Although one stabilizing carbethoxy group is present, the hydroxyl group renders the molecule unstable and it decomposes.

When heated with thoria at 400° , diethylacetal decomposes¹ giving 22 percent of acetaldehyde, 13 percent of ethyl vinyl ether, 30 percent of alcohol, 3 percent of water, a gas containing 30 percent of ethylene, 42 percent of hydrogen, 6 percent of carbon monoxide, 14 percent of carbon dioxide and 8 percent of methane. The corresponding methyl, propyl, butyl, isobutyl and isoamyl acetals over thoria decompose in a similar manner. While alumina, blue tungstic oxide and manganous oxide give similar results, the yield of the vinyl alkyl ether is smaller. Alumina and tungstic oxide give a gas containing about 95 percent of ethylene; with manganous oxide the gas contains 52 percent of hydrogen.

According to the resonance theory, catalysts with wave-lengths of $4114\text{--}2576\text{ \AA}$ induce the dissociation of CaSO_4 to CaO and SO_3 ; those with wave-lengths of $2576\text{--}1546\text{ \AA}$ cause dissociation to SO_3 , SO_2 and O_2 , while those with wave-lengths less than 1545 \AA give rise to SO_2 and O_2 , particularly at high temperature. Experiments² made with a large number of salts as catalysts confirm this theory. By using MnO_2 at 600° the yield of SO_3 can be increased from 0.18 to 25.85 percent, while the yield of SO_2 is kept as low as 54 percent. When the wave-lengths characteristic of an element and of the catalyzed substance are the same it is a sure indication that the element is a catalyst. The catalytic activity decreases with increase in wave-length. Each wave-length has a definite minimum temperature at which it begins to show its activity, and each must possess sufficient energy to decompose the molecule. It is, therefore, possible to calculate beforehand not only the direction of a reaction and its character, but also the catalyst to be used and the approximate temperature conditions.

The nature of the starting material and the temperature of reduction has been found³ to influence considerably the catalytic activity of cobalt in the decomposition of formic acid to hydrogen and carbon monoxide. The effect of temperature is not very noticeable between 200° and 300° . The activity is greatly reduced, however, when the reducing temperature is raised to 1000° , and especially so, when raised to 1200° . The activity of hydrated cobalt oxides reduced at $300^{\circ}\text{--}500^{\circ}$ is higher than for the non-hydrated oxides reduced at these temperatures.

Ruiz⁴ finds that the speed of decomposition of hydrogen peroxide in the presence of a platinum foil is inversely proportional to its potential. Previous heating in an oxy-hydrogen flame decreases the potential below the normal. The glowing of the foil thus permits its use at higher current densities without the formation of platinum oxides which exert a deactivating influence. Poisoning of the foil by CS_2 or KCN also alters the potential. Platinum exhibits its maximum catalytic influence in solutions whose pH lies between 12.2 and 12.7.

¹ Mlle. M. Cabanac: *Compt. rend.*, **190**, 881 (1930).

² Adadurov, Deribas and Kraini: *Zhur. Prikladnoi Khim.*, **3**, 509 (1930).

³ Hüttig and Kassler: *Z. anorg. allgem. Chem.*, **187**, 24 (1930).

⁴ Ruiz, *Z. Elektrochemie*, **36**, 149 (1930).

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. VI¹

BY WILDER D. BANCROFT, ROBERT S. GUTSELL,² AND JOHN E. RUTZLER, JR.³

"My first proposition, therefore, amounts to this—that the process of weaning one's-self from the deep bondage of opium, by many people viewed with despairing eyes, is not only a possible achievement, and one that grows easier in every stage of its progress, but is favored and promoted by nature in secret ways that could not, without some experience, have been suspected."

Thomas DeQuincy: "Confessions of an Opium Eater."

The cure for morphinism and other habit-forming drugs requires a well-blended knowledge of medicine, logic, psychiatry, chemistry, pharmacology, sociology, and physiology. It is not an undertaking in which one man alone can hope reasonably for success; the by-ways are far too numerous, and the main path is too obscure. It is only by clinging tenaciously to a definite idea, and constantly viewing that idea with a fresh perspective that any measure of reward has been obtained. Toil and tribulation never must cloud the road to the goal, no matter how rough it may be.

Up to the present time no one has devised a practical cure for morphinism based upon sound, scientific premises that has come into general use. That is because there has not been a generally accepted rationale for the action of morphine on living tissue. Even today the fact that morphine is both a stimulant and a depressant⁴ bewilders some good pharmacologists;⁵ because depression and stimulation have come through usage to have opposite meanings. The lack of a clear understanding of how a drug can be both a stimulant and a depressant has befogged the issue in the study of drug addiction; although it is by no means the sole reason why an eminently successful treatment has not been evolved. The purpose of this paper is to elucidate the most useful theory of drug addiction and to show that it both accounts for the facts of drug addiction and provides a rationale for the treatment of morphinism. Cases will be presented to uphold the theoretical considerations and demonstrate the validity of the theory.

There are several theories of drug addiction that are defended by various authors. Tatum and Seevers⁶ recently outlined most of them in a paper on morphinism. McGuigan and Ross,⁷ and Loofs⁸ believe that the drug is

¹ This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

² M.D.

³ Eli Lilly Research Fellow.

⁴ Sollmann: "A Manual of Pharmacology," 217 (1917).

⁵ Barbour, Gregg, and Hunter: J. Pharm. Exp. Therap., 40, 433 (1930).

⁶ Physiol. Review, 11, 108 (1931).

⁷ J. Am. Med. Assoc., 64, 1494 (1915).

⁸ Z. ges. Neurol. Psychiat., 79, 433 (1922).

destroyed rapidly or inactivated by combination, thus giving the addict tolerance. It appears to be true that the addict has developed an increased power to destroy morphine.¹ The views of McGuigan and Ross are based upon their observation that morphine sensitizes animals to strychnine if time is allowed to elapse between the two injections, and that oxidized morphine tetanizes more rapidly than morphine. They explain the usual absence of tetanus in animals by assuming that the tetanizing substance is destroyed rapidly. This explanation accounts only for the tolerance that is developed to morphine; it does not provide a useful working hypothesis. Even with the increased power of destruction of the drug the blood of the animal contains enough morphine to be toxic to normal animals.² This supposed increased power of destruction of morphine will be explained on a colloidal basis. Finally, it neglects entirely the phenomenon of abstinence symptoms during which there is a mild form of tetanus. DuMez³ says: "It has not been proved that the destruction of morphine in the organism, if it does take place to an increased degree, is a causative factor in the production of tolerance." A theory that is really usable will account for all of the facts that are observed.

Hirschlaff⁴ and others have proposed the theory that anti-bodies form after the pattern proposed by Ehrlich for proteins. These immune bodies make the cells respond to the absence of morphine and protect the cells from its action. These results generally have not been substantiated.⁵ Furthermore, we do not know of any case in which a substance, not in colloidal suspension, produces antibodies in the living organism. This theory thus can be discarded *per se*.

Light⁶ considers that the state of addiction is essentially one of imagination or wilful manifestations which are conjured up in order to enlist sympathy or to obtain more of the drug. This author believes drug addiction to be other than somatic in nature. This automatically throws the whole thing into the realm of the psychic which is erroneously considered to be apart from the brain. A complete enigma thereby is made of drug addiction. This theory is tantamount to the admission that nothing is known of drug addiction; and it bears the marks of an effort not to face the facts.

One does not imagine one's-self into a condition of complete collapse, and even death, which may be brought about by the abrupt withdrawal of morphine.⁷ So, while drug addiction and withdrawal are accompanied unquestionably by many psychotic manifestations of varying degrees of severity, there is a physical basis for the whole thing that must be faced and worked out. No amount of evangelism can evade the fact that drug addiction is a disease. Sollmann¹ says: "To the physician he [the drug addict] should appeal as a

¹ Takayanagi: *Archiv exp. Path. Pharm.*, 102, 176 (1924).

² Wells: "The Chemical Aspects of Immunity," 270 (1929).

³ *J. Am. Med. Assoc.*, 72, 1069 (1919).

⁴ *Berlin Klin. Wochenschr.*, 1902, 1149, 1177.

⁵ Pellini and Greenfield: *Archiv. Int. Med.*, 26, 279 (1920); 33, 547 (1924).

⁶ "Opium Addiction." Published by the American Medical Association (1929).

⁷ Lambert et al: *Am. J. Psychiatry*, 10, 433 (1930).

sufferer, as afflicted by a form of insanity; one who, like any other insane patient, should be treated with unflinching firmness, but with the most considerate kindness." Mr. Koepfgen of the Narcotic Educational Association of Michigan, says:

"Had the organizers of this association been willing to accept the consensus of public opinion, including governmental and medical science's findings, it is doubtful if any program of relief would have been entered into. Addicts have been catalogued as social misfits and outcasts, as hereditary mental cripples, and it is generally accepted as a fact that if they were not addicts they would occupy some other anti-social sphere. They are considered degenerates, and as leeches upon the whole social structure, sucking the life blood at every opportunity from the social, moral, and economic life. Incurable social lepers, debauched by their own viciousness.

"Society's attitude toward its addict population is reflected and magnified by the addicts' attitude toward society, an attitude equally as destructive, but founded perhaps on more reliable and understandable premises, than those of society toward the addict. We find the addict readily admitting to himself and not seldom to others, that he is a physical, mental, and spiritual wreck; admitting stealing, lying, cheating, and, if occasion demands it, being a major criminal. He is not, however, ready to agree with society that he was 'born that way.' In many, many instances, he realizes that he came from as good stock and as fine a home environment as those who condemn him. He lays claim to having possessed at one time the same physical and mental attributes as his condemners; of having had the same loves, hates, desires, ambitions and aspirations as his scornors. One thing he is sure of is that without his drug he will be sick—physically sick—with an intensity that puts to shame man's ordinary whinings over usual ailments. Let society call it a vile habit if they care to, he knows that if it is a habit it is the only habit known that causes not only mental anguish, but real physical, excruciating pain. His is the paradox of seeing organized society planning and building and caring for other sick members of society, regardless of whether or not the patient contracted his disease legitimately or illegitimately, and almost completely ignoring its addict population; extending their sympathy and charity to its animal kingdom, and yet saying to its human addict population 'So you are sick are you? Well, lie down and die and prove it, but provide your own proving ground.' If, sometimes, they do just that, it isn't too bad for the addict, it is just a blessing to society.

"The addict lives each day and dreams each night just one thing—fear. Fear, first and paramount, that he will be unable to obtain his drug to allay his illness; fear that he will be caught stealing; fear that he will be found with his medicine in his possession; and fear of the police, his associates and of himself. Society has pronounced addicts incurables and has turned the problem over to the police departments for solution; substituting a prison cell for a hospital and a warden for a physician. Society looks into its mirror and smiles with satisfaction and pride at the image reflected there, and fails to recognize

Barbour, Gregg and Hunter¹ say: "From smooth muscle experiments, Abe has introduced evidence that morphine stimulates *as it leaves the cells*, and thus gives rise to the withdrawal symptoms. Morphine cannot, however, be thought to stimulate only as it passes out, for the same object tests as used by Abe (smooth muscle of intestine, uterus, etc.) exhibit an immediate and persistent stimulation when morphine is first applied. The drug thus falls into Straub's class of substances which exhibit their effects either while entering or leaving the cell but never during chemical equilibrium with the cell environment. On the metabolic side this concept can be illustrated by Plant's demonstration in dogs of a wave of hyperglycemia on the initiation of withdrawal, similar to that which the initial dose of morphine induces. Again sweating in man commonly appears in both instances. Another example is the edema of the brain in rats which Flowers, Dunham and Barbour found most marked early in addiction and on the first day of withdrawal."

There is no question that the stimulating action of morphine as it enters the organism must be a part of the picture.² So far as "chemical equilibrium with the cell environment" is concerned, everyone knows that morphine does exert an effect when it is in equilibrium with the cell environment, though not necessarily a stimulating one.

Abe goes on to say that the intensity of the excitation produced by morphine leaving the excised organs is proportional to the rapidity with which the morphine is carried away, to the dosage of morphine that was administered, and finally to the length of time that the drug has acted on the tissues. He says: "In the same way, the gravity of the withdrawal symptoms is proportional to the rapidity with which the withdrawal takes place, to the dose used, and to the time during which the patient has been accustomed to the drug.

"The excitation produced by morphine leaving the excised organ can be completely suppressed by putting back the morphine. By administering morphine one can also make the abstinence symptoms disappear.

"The excitation produced when morphine is washed out is due to the excitation of the parasympathetic system. In the abstinence symptoms we can also observe parasympathetic symptoms (vagatonics)."

Probably it is not strictly true that the severity of the withdrawal symptoms is proportional to the amount of drug used and to the length of time it has been used. Lambert³ says: "The amount of suffering during the withdrawal period is often an individual idiosyncrasy, but the amount of drug used, length of addiction, and physical and mental condition have some bearing. The emotionally unstable types tend to exaggerate their symptoms. The greater the amount of drug used, the longer the period of addiction, also the older the addict, the more marked is the secondary cachexia apt to be and consequently the withdrawal period can reasonably be expected to be more stormy, and the recuperation or convalescence slower. However, this does not always follow, as their statements are often misleading." Again, Plant and

¹ J. Pharm. Exp. Therap., 40, 434 (1930).

² Bancroft and Richter: J. Phys. Chem., 35, 215; Bancroft and Rutzler: 1185 (1931).

³ Am. J. Psychiatry, 10, 491 (1930).

Pierce¹ have found that there is no relation between the size of the dose, the length of time that it has been used, and the intensity of the withdrawal symptoms in dogs. In this case the psychic factor is ruled out. On the other hand, tolerance to the depressant action of morphine develops more rapidly on increasing doses of the drug than on small constant doses.²

After the tissues become saturated with morphine it is probable that larger doses of the drug or administration over a longer period of time will not make the withdrawal symptoms anything like proportionally worse. The factor in the case of human beings is a psychic one; they depend on morphine more and more, and fear withdrawal more as time goes on. Many people agree that there is an upper limit to the dosage of morphine that any given patient needs; this upper limit is very roughly eight grains per day. It is only natural to assume that reversible agglomeration takes place when the tissues and the serum proteins adsorb morphine. The colloids are peptized again when the morphine leaves the tissues and serum. In the case of the nervous tissue we are probably dealing with jellies, and the whole thing may well be a question of more and less bound water; the former is equivalent to peptization, and the latter to agglomeration.

Barbour³ and his co-workers have demonstrated that the livers, kidneys, and brains of dogs addicted to morphine are dehydrated; while the blood serum tends to show hydration. Along the same line, Binz⁴ observed the agglomeration produced when morphine acted upon the isolated cerebral cortex. Barbour and his co-workers have done some interesting work on brain-water movements in morphinism and anesthesia. Unfortunately no distinction is made between water which may be present due to syneresis, and water that is adsorbed by the protein colloids. The interpretation of experiments on edema must be withheld until this distinction is made. In another paper Barbour, Hunter, and Richey⁵ say: "Withdrawal of morphine induces hydration of the blood and probably of the tissues in general. In view of this (and of empirical relief by saline purging and the like) the distressing symptoms of withdrawal in man appear closely related to tissue hydration."

In brief review the theory of chronic morphinism as it stands at present is that the drug goes into the blood stream, and thence to the protein colloids of the nervous systems and the blood serum; the central nervous system is apparently affected first. The ratio of morphine taken up by the tissues to morphine adsorbed by the blood serum is small. The adsorbing capacity of the serum proteins is large; and, as the concentration of morphine rises, the serum proteins adsorb more of it, thus keeping the ratio small. The proteins of the nervous system become saturated first. The morphine which is adsorbed by the protein colloids causes reversible agglomeration, or its equiva-

¹ J. Pharm. Exp. Therap., **33**, 329 (1928).

² Tatum, Seevers, and Collins: J. Pharm. Exp. Therap., **36**, 452 (1929).

³ Barbour et al: Am. J. Physiol., **90**, No. 2, October (1929); Barbour: Science, **73**, 346 (1931).

⁴ Gwathmey: "Anesthesia," **34** (1914).

⁵ J. Pharm. Exp. Therap., **36**, 251 (1929).

lent, the loss of bound water. Above a certain concentration, different for each individual, the tissues and serum do not adsorb appreciably more morphine. There is a period of excitement corresponding to the initiation of agglomeration. Upon withdrawal, morphine leaves the tissues and blood stream slowly and peptization takes place gradually, or the equivalent, more water is bound, giving rise to excitement which is manifested by withdrawal symptoms. In the course of time the peptizing agents normally present in the body return the nervous systems to their correct degree of dispersion; and the patient recovers. Endocrine or other disturbances that either pre-existed morphinism, or were brought about by it, may call forth agglomerating agents which will retard materially the return to normal.

There are roughly thirty different ways that have been used to treat drug addiction, all of which aim at amelioration of withdrawal symptoms. The after-care is generally considered to be a different problem. Lambert¹ has studied many of the methods of treatment; and has made a very complete report on the subject. Some of the methods that have been used can be considered here in some detail. It is not either useful or necessary to take up the use of magnesium sulphate (as an anesthetic), allonal, ravenin, bromides and chloral, sodium luminal, alcohol, paraldehyde, veronal, trional, and pyramidon in the treatment of drug addicts. Each of these is an agglomerating agent for the protein colloids of the nervous systems, and as such can only act in the same direction as morphine, thus making the problem harder. Sodium bromide has been given with chloral under the mistaken impression that they are both sedatives. Sodium bromide merely quiets the nerves by peptizing the colloids out of their irritable state, and allows one to go to sleep; whereas chloral hydrate puts one to sleep by agglomeration. Lambert found that none of them were of any particular benefit during the withdrawal period, as one would expect from the theory.

The treatment by the use of Narcosan, a mixture of lipoids, non-specific proteins, and water-soluble vitamins, apparently aggravates the withdrawal symptoms. This drug is apparently of very little benefit² since it generally increases the suffering of the patient. Atropine and aspirin were both found wanting so far as the alleviation of suffering is concerned.

Hyoscine treatment is designed to allay the discomfort of withdrawal by throwing the patient into a delirium. However, addicts claim, and Lambert found, that this drug does not help the patient, despite the delirium. It was found that codeine, which is in the morphine series of alkaloids, can be substituted for morphine during the gradual withdrawal of the latter. Codeine does lessen the withdrawal symptoms. Since codeine undoubtedly works in the same direction as morphine, this form of treatment is merely a leap from the fire into the frying pan, although one does not become habituated to codeine so easily as to morphine.

¹ Lambert et al; *Am. J. Psychiatry*, 10, 433 (1930).

² Lambert et al; *Am. J. Psychiatry*, 10, 433 (1930); Nellans and Masse: *J. Am. Med. Assoc.*, 92, 1153 (1929).

Sodium amytal has been used in the treatment of drug addicts; the thought being that the patient could be rendered almost unconscious by the drug due to its anesthetic action. In this way withdrawal symptoms might be obliterated. This should not be the case unless the patient is deeply anesthetized, because sodium amytal and morphine are both agglomerating agents, and act in the same direction. Lambert, p. 525, says: "Seven of the twelve patients showed considerable irritability both during and after treatment. It was also found that where the patients became disturbed under the use of amytal further doses accentuated this restlessness, rather than diminished it. . . .

"The disturbed cases thrashed about in a state of motor restlessness and mental confusion and delirium. The typical symptoms of barbituric acid intoxication were apparent in the ugly, irritable frame of mind of the patient, the staggering gait, and slurring and ataxic speech, and mental haziness.

"In a few cases marked psychomotor excitement manifested itself." It was found that the withdrawal symptoms were not ameliorated by sodium amytal and that recuperation was slightly delayed.

These findings were quoted because it is worthy of note that the effects found can all be predicted on the basis of the theory of reversible agglomeration in living tissue.

In other cases Lambert's Committee used psychotherapy to some avail. This will be discussed under another heading. Potassium permanganate was found to be of no use in treating drug addicts. Strychnine and parathyroid extract in different sets of experiments did not alter the withdrawal picture.

Concerning alkalies Lambert's report, p. 529, says: "As mentioned previously, sodium bicarbonate in 30 grain doses every four hours is often beneficial to patients undergoing abrupt withdrawal treatments, as the marked gastro-intestinal symptoms incidental to these methods of withdrawal and the semi-starvation often produce a condition resembling acidosis with acetonuria [which condition is probably an aid to the agglomeration that has caused the addict all of his trouble] and the alkali also reduces the subjective sensations of 'heartburn' and abdominal cramps." They found that sodium bicarbonate was more effective than magnesium oxide.

Abrupt withdrawal, when the patient can stand up under it, or seven or fourteen day reduction treatments are recommended by Lambert as a result of his exhaustive study. None of the drugs studied helped materially in making the withdrawal period easier.

Nellans and Masee¹ mention three other methods for the treatment of drug addiction. The Pettet treatment uses forced fluids, vapor baths, atropine, scopolamine, and other sedatives along with spartein sulphate and sodium thiosulphate. Spartein is apparently also an agglomerating agent, since it has a strong curare action, paralyzes the respiratory center, and has a weak local anesthetic effect.² The Jennings treatment consists of the use of ethylmorphine hydrochloride in the place of morphine and spartein sulphate. The Scelet method of treatment is by the administration of a mixture that

¹ J. Am. Med. Assoc., 92, 1153 (1929).

² Sollmann: "A Manual of Pharmacology," 318 (1917).

would scare anyone: scopolamine, pilocarpine, ethylmorphine hydrochloride, cascara sagrada, and alcohol. Strychnine is used for good measure. Nellans and Massee recommend the abrupt withdrawal treatment.

E. H. Williams and co-workers¹ have used alfalfa protein by injection in the treatment of drug addiction, the method being called the proteal treatment. It is designed to replace Narcosan in withdrawing drug addicts. In this report the statement is made that: "We disagree with this clinical deduction [that there are toxic substances of a definite character in the blood as a result of chronic morphinism or withdrawal] because it seems to us that the evidence presented by the clinical picture of addiction, and certain chemical features, indicate primarily rather a disturbance of the endocrine system—either primarily or secondarily to the sympathetic nervous system. There is no question about the endocrine hypo-function in these cases, as indicated by the lowered blood pressure, low basal metabolism, and generally weakened condition which may be improved by direct action of endocrine substances." Undoubtedly the above statement forms an important part of the picture of drug addiction. Further on they say: "In addition to this treatment primarily, we found it expedient to keep the patient alkalized with sodium bicarbonate, and, to combat the inevitable nervousness, we administered strychnine. . . . as suggested by Lambert and Tilney in their narcosan treatment. Strychnine was the sheet anchor of the treatment given by the late Dr. Bishop and its value is recognized by everyone who attempts the treatment of drug addiction." Williams found orchitic substance to be useful in his treatment. The paper does not point out clearly that the proteal treatment has a very definitely better effect on the patient than does Narcosan, which is worse than nothing.

Strychnine seems to be quite widely used in one way or another in the treatment of drug addicts. Lambert pointed out that it does not help the patient. Sollmann² says that the bitter and tonic effects of strychnine make it useful in the treatment of chronic alcoholism and other drug habits. He also says that morphine is theoretically objectionable as an antidote to strychnine because its action on the spinal cord is synergistic to strychnine. "It has been employed, however, and its analgesic action at least would be useful." It seems best, for the time being, to assume that strychnine merely soothes the gastro-intestinal tract to a small degree during withdrawal.

In another method of treatment³ profuse catharsis, very hot baths and salicylates are used during a ten to fourteen day withdrawal period. Bancroft and Rutzler⁴ have discussed MacLeod's use of the peptizing agent sodium bromide in the treatment of drug addicts.

Poppe⁵ succeeded in mitigating the withdrawal symptoms by the use of ephedrine hydrochloride in three addicts who were given abrupt withdrawal.

¹ Med. J. and Record, September 7, 1927.

² "A Manual of Pharmacology," 194, 197 (1917).

³ Sollmann: "A Manual of Pharmacology," 236 (1917); Drysdale: Clev. Med. J., 14, 353 (1915).

⁴ Proc. Nat. Acad. Sci., 17, 186 (1931).

⁵ Klin. Wochenschr., 7, 775 (1928).

Since ephedrine is a good peptizing agent¹ and acts upon the sympathetic nervous system,² which is disturbed during withdrawal, its successful use, barring side reactions, is to be expected. Undoubtedly it will be used more as time goes on.

In résumé, many of the treatments devised for use on the drug addict during withdrawal make use of agglomerating agents which are worse than useless in an already agglomerated condition. The only treatments that have merit from the view-point of the present theory are those that employ sodium bicarbonate, sodium bromide, ephedrine, or withdrawal without drugs. As yet, the real problem that is involved has not even been touched upon. It matters not by what method withdrawal is accomplished, or whether or not a severe reaction occurs. The important and pressing thing is to bring about normal nervous, physical, and mental stability. It appears that people have been too busy trying to devise means for painless withdrawal.

Mr. Koepfgen, who probably has the best treatment that there is in this country for drug addicts, says:

"In administering treatment for addiction, this Association has always recognized the problem as more than a habit problem. We have looked upon it as a problem requiring not only medical treatment, but as one requiring also a physical, mental, moral, and spiritual rehabilitation; a problem that cannot be solved in a few short weeks, but one that requires months; medical treatment over a short period and a long time rehabilitation period conducted under thoughtful, conscientious, and sympathetic administration; a treatment administered under conditions as near ideal as possible where the sufferer can be removed from his usual environment and temptations; a treatment which can be conducted in the open where outside labor and recreation can be furnished and where a normal routine of activity and methods of living can be had, and where the mental and spiritual life can be studied and administered to. Society does not attempt the cure of blood poisoning in a room infested with scarlet fever. Why then should attempts be made to cure drug addiction under less favorable conditions?"

It seems advisable to consider the mental condition of drug addicts from the point of view of reversible agglomeration.

Jelliffe and White³ say: "The habitual use of opium in some form has become common among all classes in society. The same thing may be said with reference to the reasons for taking opium as has been said with reference to alcohol." Under the psychology of alcoholism they say: "People drink because of definite returns which they get from drinking. . . . When the individual is confronted by situations to which he cannot adjust adequately, when the world of reality makes demands which are too great for him to meet, one of the ways in which the individual reacts to such a condition is by narcotizing himself and so withdrawing from the whole situation. . . . The moment the individual, harassed by the absolutely unacceptable demands of

¹ Bancroft and Rutzler: *J. Phys. Chem.*, **35**, 3189 (1931).

² Chen and Schmidt: "Ephedrine and Related Substances," (1930)

³ "Diseases of the Nervous System," 1073 (1929).

the world, finds an avenue of escape in which he can rest from their harassings, finds the possibility of peace, of repose, he finds it equally impossible to resist the temptation to avail himself of it. He is rendered more and more incapable of meeting the conflict efficiently. Therefore a vicious circle is established and the individual is hopelessly involved."

Further on they say: "Aside from the class of individuals described above, it must be constantly borne in mind that indulgence in alcohol is oftentimes the expression of a neurosis or a psychosis. For example, the recurrent attacks of manic-depressive may be ushered in by alcoholic indulgence, and if one is not keenly observant he may easily suspect that he is dealing with an alcoholic psychosis rather than with a manic-depressive. The same thing of course may be said of dementia praecox."

"It is these¹ less well differentiated types of emotional and volitional deviations which are to be designated, at least for statistical purposes, as psychopathic personality. The type of behavior disorder, the social reactions, the trends of interests, etc., which psychopathic personalities may show, give special features to many cases, e.g., criminal traits, moral deficiency, tramp life, sexual perversions and various temperamental peculiarities.

"In accordance with the standpoint developed above, a psychopathic personality with a manic-depressive attack should be classed in the manic-depressive group, and likewise a psychopathic personality with a schizophrenic psychosis should go in the dementia praecox group."

In discussing constitutional inferiority, Jelliffe and White say: "This type not infrequently suffers psychotic episodes where for any reason, such as conscription or imprisonment, they are prevented from slipping from under responsibility or running away from reality. Often at the slightest stress, such as a strong effort to make good, business reverses or loss of a loved object they develop paranoid symptoms, deep depression, or take to alcohol or drugs." These authors say that when a psychosis develops as the result of the use of opium it is characteristically a hallucinated state; and there are usually paranoid symptoms. In view of the theory of reversible agglomeration in living tissue, it is worthy of note that alcohol and morphine, both of which are agglomerating agents, may bring about paranoid conditions. Also, in general paresis and dementia praecox paranoid, which are accompanied by agglomeration,² there are delusions of grandeur. According to Dr. Lang³ the hypomanic state is an imbalanced, agglomerated one. The hypomanics frequently become drug addicts in civil life because morphine has a definite sedative action. Their first response to sedative drugs, which act by agglomeration, is usually an improvement, because they then can concentrate better on a lesser number of stimuli received. Because of the psychomotor hyperactivity and flight of ideas that one often observes, in some salesmen for instance, it is felt that they have a tendency to be in a condition akin to the hypomanic state of the manic-depressive psychosis. In the rehabilitation of drug addicts it is very important

¹ "Statistical Guide, New York State Department of Mental Hygiene," 22 (1930).

² Lang and Paterson: *J. Phys. Chem.*, 35, 3425 (1931).

³ Private Communication.

to recognize tendencies toward one type of psychosis or another in order that the proper kind of treatment (mild peptization or agglomeration) may be used during rehabilitation.

It can be seen that in the case of the drug addict there are all sorts of possibilities; the drug may have been taken originally in response to: a schizoid type of personality with or without a definite psychosis, a cycloid type of personality with or without a definite psychosis. In other words, the individual may have had a mental condition that involved either over-dispersion or agglomeration of certain of the protein colloids of the brain. In each case, the type of post-withdrawal treatment is necessarily different. Of course, the first thing that must be accomplished is peptization; for in either case morphine will cause abnormal agglomeration if it is used for any length of time. By the time that the nervous systems are returned approximately to normal by peptization, the decision must be made as to whether the patient was originally over-dispersed or agglomerated. Mental rehabilitation can then be carried out by the use of the proper drug.

Lambert¹ says: "As we have mentioned, as a class drug addicts are very suggestible, and many of their real or imaginary symptoms are often relieved by suggestion properly applied. Sterile hypodermics containing saline or plain water were given to twenty-five patients at various times with frequent quieting effect."

Dr. Stolper² says that those suffering from dementia praecox paranoid are extremely suggestible. This is probably a well-known fact. At any rate, the comparison is interesting.

So, here we are in 1932 with no drug that is generally recognized as being of real value in alleviating the suffering during the withdrawal of narcotics from addicted persons. Worse still, with the exception of the work of Dr. Stokes in his colony at Warwick, New York and Mr. Koepfgen in his colony near Detroit, no intelligent plan known to us has been devised for the mental rehabilitation of drug addicts. And it should be emphasized that the only really important thing is mental rehabilitation; it makes little or no difference how the drug is withdrawn.

The theory of reversible agglomeration in living tissue, including particularly the work of Drs. Lang and Paterson, makes it possible to use certain drugs during the post-withdrawal treatment that theoretically and practically aid mental rehabilitation. If the patient merely wants morphine when he has recovered from the withdrawal, and has no physical need for it, the problem is a serious one to which much time, thought, and energy must be given. This type of patient must be given institutional care and the proper drugs along with "brain drill" for a period of several months in order to change his mental habits; he must be taught to face reality and depend on himself. The problem is a simple one if the patient is merely in a state of nervousness and is bothered by insomnia; because in this case the proper dosage of a peptizing agent will restore him to normal. If the individual took drugs originally because of some

¹ Am. J. Psychiatry, 10, 528 (1930).

² Private Communication.

mental condition that was accompanied by over-dispersion, treatment with a peptizing agent should help him through the withdrawal period. Continued use of the dispersing agent should then cause him to resume the drug because of a return to his original mental condition, even perhaps to an aggravated form. Where there is a manic-depressive psychosis or tendency, or a paranoid coloring to be dealt with, peptizing agents will tend to restore the patient to normal both as regards the mental upset and the after effects of drug addiction. The individual who is best described as a "pathological thrill-seeker" presents another difficult colloidal problem.

In this study no attempt has been made to standardize the treatment of drug addicts with a peptizing agent; no effort has been made to use the best possible peptizing agent. The main purpose has been to employ a drug that must act primarily as a peptizing agent for agglomerated protein colloids, and to show that it can be used successfully, thus supporting the general theory.

Cases will be reported in chronological order including both successes and failures. Even the failures have taught us much regarding the application of the theory.

Case 1, J. H.

Early in the year a brief report² was made on this particular patient. Since a detailed report is desirable, and since much has transpired since that time, the case must be considered here.

The patient was a male nurse, forty-nine years of age. He had been addicted to the use of morphine for a period of sixteen years. The reason given for his initial addiction was that he was given morphine for several weeks to allay the pain of an abscessed kidney. Before coming to us he had been withdrawn from the drug about six times by various methods: insensible withdrawal, rapid withdrawal, abrupt withdrawal, and the Towns-Lambert treatment. The patient returned to the use of morphine every time but once within a period of one to two weeks because of weakness, insomnia, and nervousness. After one of his withdrawals the patient abstained from morphine for a period of about four months. The interesting thing here is that he used large quantities of sodium bromide during that time. The peptizing action of the sodium bromide undoubtedly kept the patient from returning to the use of morphine. The sodium bromide produced a rash which caused him to discontinue its use, with the result that he again began to use morphine.

The patient was not a good risk from the start because after withdrawal he had no prospects of employment, little money was available to him; and he had an aged and ill mother to care for in surroundings that were not of the best. The natural prospect was that the combination of circumstances would prove to be too much for him. In addition he was a manic-depressive depressed.¹ During the time that he was under observation in connection with this study, hypomania was the only indication of a psychosis that was observed.

¹ Bancroft, Gutsell, and Rutzler: *Proc. Nat. Acad. Science*, 18, 8 (1932).

² Private communication from Willard State Hospital.

The patient was admitted to the Ithaca Memorial Hospital¹ on November 30, 1931, at which time he claimed to be using twelve and one-half grains of morphine a day by intravenous injection. Upon admission to a private room, the patient's clothing and belongings were thoroughly searched before being placed under lock and key. A hypodermic syringe and needle were removed and disposed of. No morphine was found. He was put to bed at this time, and not allowed to be up except for short intervals, during which time he did not leave his room, until three days after morphine was discontinued. No visitors, except members of his immediate family, were allowed to see the patient. When visited by members of his family, the nurse in attendance was present all of the time with rigid instructions to prevent any drugs from being given to the patient. He was not allowed to have any packages; and the two or three letters that came were scrutinized carefully before delivery to him.

Physical examination revealed retracted gums which accompanied gingivitis. The prostate gland was slightly boggy and slightly enlarged in the left lobe. There was no tenderness. The skin was smooth, white, and dry with numerous discolorations of the arms and thighs where hypodermic injections had been made. The knee jerks were active and equal. The patient was thin but not emaciated; there was only a small amount of subcutaneous fat. The other physical findings were negative.

It was learned that the patient had a severe constipation while taking morphine. He had nocturia about twelve times a night.

The following plan was made for the experiment. The patient was to be studied for two or three days prior to the initiation of withdrawal of morphine. The drug was then to be withdrawn as rapidly as consistent with physical comfort, at the same time using enough sodium rhodanate, administering it in a water solution by mouth, as needed, to allow the withdrawal to be accomplished rapidly without too much discomfort.

December 1, 1932.

The patient slept only at intervals and between 1:00 a.m. and 6:00 a.m. His appetite was very good in the morning. He smoked cigarettes incessantly; he was calm with an apparent substratum of nervousness and apprehension. The patient quieted down during the evening. He had a fairly comfortable day; he was rather restless before midnight. The nocturia of which he complained was manifested. During the twenty-four hour period he was given six grains of morphine sulphate by subcutaneous injection. It would appear from his restlessness that he has been used to a larger quantity of the drug than this.

December 2, 1931.

The patient was very restless during the early morning hours. When given morphine he quieted down and slept fairly well from 2:00 a.m. to 6:00 a.m. He had a fairly comfortable day, being more quiet and less apprehensive. He did not concentrate so well as he did on December 1. These changes prob-

¹ The Hospital placed at our disposal a limited number of beds for a limited length of time, for which we are duly grateful.

ably resulted from the twelve grains of morphine that were administered during the last twenty-four hour period. During the afternoon the patient was given an enema; and at night two Alophen tablets were administered. He was uncomfortable during the forepart of the evening.

December 3, 1931.

Morphine reduction was started on this date. The patient passed a fairly comfortable night. His appetite was very good during this day. The day was an easy one for him; he was only slightly nervous, and not apprehensive at all. He concentrated better than before. He talked incessantly when given the opportunity. At times he would, without provocation, try to convince those attending him that his family was respectable, he was honest and not murderous, even though he was an addict. At times he became argumentative. The manic-depressive characteristics of the patient were beginning to come to the surface. It did not require close observation to see that the patient was very jealous of his own personal comfort. He was quiet, friendly, cooperative, and popular.

The patient slept a little during the day, and for a long time during the evening. At this time it was decided to administer equal quantities of morphine by hypodermics at regular intervals during each twenty-four hour period. They were given at 5:00 a.m., 11:00 a.m., 5:00 p.m., and 11:00 p.m. Sodium rhodanate was given at 6:00 a.m. and 10:00 p.m., and as needed. Table I shows the daily dosage of morphine, and of sodium rhodanate during the withdrawal period.

TABLE I

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
12-1-31	6	0	12- 6-31	2.5	1.33
12-2-31	12	0	12- 7-31	1.0	1.10
12-3-31	7.5	0.67	12- 8-31	0.62	3.00
12-4-31	6	1.33	12- 9-31	0	3.8
12-5-31	4	1.33	12-10-31	0	1.5

December 4, 1931.

The patient slept well all night. His appetite continued to improve. When visited at 11:00 a.m. he was very much relaxed; he was neither nervous nor apprehensive. The patient made the remark that some of the wrinkles had gone out of his face. There was a definite change in this respect which was probably due to the nervous relaxation afforded by the sodium rhodanate. The relaxation persisted throughout the day. During the afternoon he slept off and on; he yawned a great deal. The yawning was not a withdrawal symptom. It was due in all probability to the fact that when truly relaxed he found that he was tired.

The pupils were contracted; and there was no change to date. The patient was somewhat uneasy before his hypodermic at 5:00 p.m. After the injection the patient said that he could not feel the morphine "take hold." It goes

without saying that in this case, and each of the others, the patient was not told how much morphine was being administered. They always received the same volume of solution from the hypodermic syringe. The five o'clock injection did not quiet the patient very much; he was only very slightly restless. The secretions from his nose and eyes increased somewhat. The patient did not complain at any time during the day. One hour before the morphine was administered in the evening, ten grains of sodium rhodanate were given. The patient said that the 11:00 p.m. hypodermic "took hold." Thirty minutes after the sodium rhodanate was given the patient was very definitely more quiet. The increased secretions subsided. He was given two Alophen tablets during the evening. By 11:30 p.m. the patient was asleep.

December 5, 1931.

The patient slept well after 11:30 p.m. last evening. His appetite was good again on this date. During the basal metabolism test at 8:00 a.m. the patient was kept awake only with difficulty. Sodium rhodanate was given one hour before morphine was administered on this date. The patient was more composed than he had been at any time since entering the hospital; he was somewhat less talkative and appeared to be mentally and physically normal. He was much quieter than formerly, and was not at all apprehensive. At noon he was extremely comfortable.

During the afternoon he slept a great deal. At 4:00 p.m. he was very relaxed and quiet, as compared to slight nervousness at that time on December 4. During these five days the patient slept more each night. The pupils of his eyes remained contracted. At night he was given two Alophen tablets; the physic had not worked to date. The patient put in a very comfortable day. He slept from nine o'clock in the evening to twelve o'clock.

December 6, 1931.

Except for short intervals, when he was awakened to be given medicine, the patient slept from midnight until 6:30 a.m. He had a comfortable night, and slept soundly. Relaxation and quiet were the order of the morning. At noon the patient complained of cramps; it was thought at first that this was a withdrawal symptom. He then said that he had not had a bowel movement for three days. At 1:00 p.m. a good bowel movement made the patient feel better; and the cramps disappeared.

About 3:00 p.m. the patient became somewhat nervous. He said that there were darting spots before his eyes. The patient stated that he could tell during past withdrawals to within one-sixteenth grain how much morphine he was being given. On the assumption that he could tell perhaps to one-eighth grain¹ how much drug was being administered, he was asked to guess the amount being given at each dose. The patient was unable to tell anything about how much morphine was being administered per dose. He could not even form an opinion. At various times, as the reduction continued, the patient was asked to guess how much morphine there was in each

The patient was given one-eighth of a grain of morphine at 4:20 p.m. This cleared him quite a bit mentally, but left him quite intoxicated. He was slightly irrational, and quite restless. This restlessness was almost entirely a motor reaction so far as could be determined. There seemed to be a strychnine-like action on the cord. In fifteen minutes the patient was much clearer and not so restless. He refused food at 5:00 p.m., although he had taken little nourishment all day. At 6:20 p.m. he was given fifteen grains of sodium rhodanate; the patient was still agitated at seven o'clock, at which time he ate toast and jello, and drank tea. A two cc. sterile saline hypodermic containing a few drops of a 5% solution of novocaine was administered. The novocaine was added so that the local anesthetic effect of morphine would be simulated. This quieted the patient for about fifteen minutes, which demonstrated that a large part of his trouble was mental.

The patient became restless and nervous again at 8:10 p.m.; he was in and out of bed a good deal. Petrolagar was given at this time. At nine o'clock he pled for an injection of morphine to be given instead of at eleven o'clock. A saline hypodermic was administered as before. This made him easier for a few minutes; the patient then insisted that the injection did no good. At 9:30 he was given seven and one-half grains of sodium rhodanate; he was very restless at that time. One-eighth grain of morphine was administered at 11:00 p.m. The patient expressed the fear that there were many days of suffering before him, as had usually been the case. He guessed, shortly afterward, that he was being given one-quarter of a grain of morphine at a dose; whereas, he was only getting one-eighth of a grain. He was told that one-eighth grain doses were being given; at first the patient refused to believe this. When he was convinced that that was the case, a wide grin came over his face, he turned over in bed, and said that we would not hear another word out of him. The patient quieted down markedly and dozed for about ten minutes after volunteering the information that a difficult time is in order when the last one-half grain of morphine is withheld. Upon wakening, the patient had a good appetite which was satisfied. It seems perfectly fair to assume that much of the restlessness that the patient exhibited was due to the fear that he was faced by many days of discomfort before the morphine was completely withdrawn. He volunteered the information that had it not been for the sodium amytal he would have had a fair day.

Later on it was learned that the afternoon and evening of this day were a blank in the patient's mind. Only very slight gastro-intestinal symptoms were observed; they took the form of nausea during a part of the morning.

December 9, 1931.

Just after midnight, the patient appeared to be somewhat depressed; he was uncommunicative. He did not want to be bothered, for he desired to sleep. At 2:00 a.m. the patient was awake, restless, and very talkative. He was in the hypomanic state again. An hour later, he was up and about; he perspired a little for a short time. It should be borne in mind that the patient perspired only at such times as are mentioned in this record, and then

only for fifteen to twenty minutes. Between 3:30 and 4:30 a.m. the patient slept for brief intervals. Ten grains of sodium rhodanate were administered at 4:30 a.m. Although he continued to be restless, the patient slept better from that time on. Petrolagar was given at 6:00 a.m.; this was used in an attempt to keep the bowels open and at the same time avoid diarrhea.

At eight o'clock the patient ate a hearty breakfast. He was not depressed; and his mental condition was much improved. He was restless for short periods of time; his elbows and buttocks were red from the friction of contact with the bed. The patient complained of feeling as though worms were crawling around in his abdomen. No tremors were found. This sensation was relieved by ten grains of sodium rhodanate, given at 10:00 a.m. The pep-tizing agent quieted the patient definitely. At about this time his face became flushed—vasomotor instability—which reaction subsided in fifteen minutes.

Definite auditory hallucinations, mental discontinuities, and hallucinations of sight were exhibited each time that the patient was on the verge of sleep, either just as he was dropping off, or upon awakening. These symptoms, and those that some of the other patients exhibited, will be discussed in detail further on.

A brief wave of restlessness passed over the patient at 10:30 a.m. At 5:00 a.m. and again at 11:00 a.m. the patient was given a sterile saline hypodermic containing a few drops of novocaine solution. He did not ask for these injections. At noon the patient ate a good-sized dinner; he was fairly quiet all afternoon. At 5:00 p.m. the patient protested that he did not want the hypodermic, despite the fact that he believed that it contained a little morphine. He slept from seven to eight o'clock in the evening.

By nine o'clock in the evening the patient was very quiet; he did not talk a great deal, except when he was addressed. He gave the appearance of being mentally drowsy and relaxed. He was incredulous when told that no morphine had been administered for twenty-four hours. The patient slept lightly from 10:30 p.m. until midnight. During his nervous spells on this date, the patient experienced no difficulty in staying in bed. It was somewhat difficult to fix his attention during the daytime. The patient exhibited slight muscular twitching during a large part of the day; this did not seem to bother him. Since, according to Sollmann, morphine has a strychnine-like action on the cord, the assumption is made that the rhodanate ion threw the morphine off of the protein colloids of the sensory nerves before those in the cord. The sedative action of the morphine was counteracted thereby, the result being the strychnine-like action. In the usual case when there is twitching, the morphine has merely left the sensory nerves more rapidly than it has the cord.

December 10, 1931.

Shortly after midnight, the patient exhibited a wave of depression which soon passed off. At no time did these periods of depression last for more than twenty to thirty minutes; furthermore, they were not observed to occur often. There was never any severe depression. The patient was very quiet all

night long, although he only slept at intervals. No request was made for morphine. In the morning his appetite was better; he was rational. The patient was absolutely calm, comfortable, and collected during the whole day; he stayed in bed, and did not exhibit any signs of nervousness or restlessness. The nervous tension was gone from his face. He was not depressed. So absolutely quiet was he that several physicians who saw him refused to believe that no morphine was being administered. That was the first of a series of grave mistakes that certain physicians made where this case was concerned. The patient had six bowel movements during the day. He slept during the evening. No hypomanic symptoms were seen during the last twenty-four hour period; thirty grains of sodium rhodanate were given in this time.

From this point on a very brief clinical summary will illustrate the reactions that the patient underwent.

December 11, 1931.

Shortly after midnight the patient vomited an emesis basin full of dark vomitus. A hot water bottle was applied to the epigastric region; this made the patient feel better and he fell asleep almost immediately. He had a comfortable night, and slept well. At no time during the course of this study did the patient become hyper-sensitive to heat or cold. Under all other treatments the patient did become hyper-sensitive to heat and cold. The patient was quiet and composed all day long. Thirty grains of sodium rhodanate were administered in the last twenty-four hours. No withdrawal symptoms were noticed. The bowels were normal.

December 12, 1931.

The patient slept soundly for eight hours. In the middle of the morning he was taken outside, away from the hospital, for two hours. During this time he vomited bile once. He felt nauseated after supper. Because sodium rhodanate may upset the stomach at times, administration of the medicine was changed so that it was given before meals. The patient was not nauseated thereafter. He passed a comfortable, quiet day. Twenty-five grains of sodium rhodanate were given during the twenty-four hour period.

December 13, 1931.

The patient slept at long intervals during the night. The hypomanic condition was observed less and less as the days progressed. The clinical observations for the day were negative, except for a rise of nervous tension during the late afternoon and evening. The patient was not uncomfortably nervous. The nervousness is accounted for by the fact that the patient was only given fifteen grains of sodium rhodanate, five of which were given at 6:00 a.m. and ten at 10:00 p.m. He needed more of the medicine than this to keep him comfortable.

December 14, 1931.

That he did not have enough sodium rhodanate on December 13, was shown again by the fact that the patient did not sleep well during the night. He complained bitterly about not sleeping well. That brings up a very im-

portant point which must be considered carefully. Insomnia leads many addicts back to the drug that they were using. This patient returned to morphine on several former occasions because of insomnia, after having been withdrawn. The patient slept less as the dosage of sodium rhodanate was decreased. This means that he did not stay peptized sufficiently. Certain of the sensory nerve colloids bordering on a state of agglomeration gave rise to irritability which kept the patient awake. If, at this time, the patient had been given an agglomerating hypnotic, it would have tended to cause more agglomeration of the protein colloids of the nervous systems. This would have started him back almost surely on the road to morphinism, because his original addiction was due partly to nervousness and hypomania, which are generally agglomerated conditions. Sodium rhodanate, in the correct amount, will quiet the sensory nerves by peptization and *allow the patient to go to sleep*; whereas, such drugs as chloral hydrate, allonal, veronal, sedormid, and sodium amytal put one to sleep by agglomeration. That is where mistakes have been made in the past. At the same time, it should be emphasized that too much sodium rhodanate will keep one awake due to over-peptization of certain protein colloids in the brain. In such cases either the peptizing agent can be discontinued temporarily, or an agglomerating drug used. It is very important to determine in any given case which kind of sleeplessness one is dealing with in order to employ the correct medication.

Since the patient was not being given enough sodium rhodanate, especially at night, none was given until 10:00 p.m., when thirty grains were administered. He slept lightly for two hours thereafter. He was neither depressed nor nervous. Using the ferric chloride test, sodium rhodanate could not be demonstrated in the blood serum. This may be of very great importance, indicating, as it does, that the tissues took up most of the drug. A slight nervous cough was noticed during the day.

December 15, 1931.

A very uncomfortable night was passed by the patient. He was neither restless nor nervous; but he was very much upset mentally, because he did not sleep well. Having decided from the theory that the patient was not being given enough sodium rhodanate, the only thing to do was to continue the larger dosage until the desired result was accomplished. It was quite evident that if this problem was not solved satisfactorily, the patient would soon return to the use of morphine. At 1:30 p.m. five grains of sodium rhodanate were given. He was then taken for a long walk in an attempt to tire him. The desired results were accomplished; he had an excellent appetite and felt like sleeping. At this time, he began to complain of feeling weak. He was extremely jealous of his own comfort.

The patient was given twenty-five grains of sodium rhodanate at 9:00 p.m. He fell asleep immediately thereafter, and slept soundly until midnight.

December 16, 1931.

The patient slept soundly for seven hours. He spent a quiet, comfortable day; he was taken for a walk during the afternoon. His appetite was fair, but not voracious. Five grains of sodium rhodanate were given at 2:00 p.m., and twenty-five grains at 9:50 p.m.

December 17, 1931.

The patient slept soundly during the night. The problem of sleeping apparently was solved. He spent a quiet, comfortable day. He still complained of feeling weak when taken out for a walk. Twenty-five grains of sodium rhodanate were given at 8:00 p.m. The patient slept soundly from nine o'clock until midnight. There were no signs of nervousness.

December 18, 1931.

A good night's sleep was had by the patient. In the evening, he complained of feeling weak and tired. The day was a quiet, comfortable one. Twenty grains of sodium rhodanate were given at 8:00 p.m. He slept from 8:45 until midnight.

December 19, 1931.

The patient passed a comfortable night, and slept well. During the rest of his stay at the hospital, it was impressed upon him daily that alcohol, sedatives, nervous exhaustion, and the like would lead him back to morphine. He was informed that in times of distress, no matter what its nature, he should come immediately to those who treated him.

In the afternoon the patient was shown a list of the common withdrawal symptoms. He looked the list over, and became very nervous. Perspiration broke out all over him; he became flushed and felt it necessary to lie down. The reaction subsided in fifteen minutes. This was a good illustration of the extreme suggestibility of the patient.

At 8:00 p.m. twenty grains of sodium rhodanate were administered; an effort was being made to reduce the amount of the drug administered daily. The patient slept from 9:00 p.m. until midnight.

December 20, 1931.

Twenty grains of sodium rhodanate was not quite enough to afford the patient a long sound sleep. Considering his relative inactivity seven hours of sleep should have been adequate. During the latter part of the treatment, the patient was taken out for a short walk every day. Fifteen grains of sodium rhodanate were given at 8:00 p.m., after the patient had had a comfortable day.

December 21, 1931.

The patient slept well during the night. Except for a short period of nausea at 10:30 a.m., this day was uneventful. Ten grains of sodium rhodanate were administered at 8:00 p.m.

December 22, 1931.

After a comfortable night during which he slept well, the day was uneventful. Seven and one-half grains of sodium rhodanate were administered at 8:00 p.m.

At this time during the treatment the hypomanic characteristics of the patient had practically disappeared. The psychomotor hyperactivity and flight of ideas had subsided. The patient smoked very little as compared to almost continually in the beginning. He had lost his taste for cigarettes. The sodium rhodanate made them taste bad. He still complained of feeling weak.

December 23, 1931.

The patient was somewhat restless during the night; this was probably due to the smaller amounts of sodium rhodanate that were being used. The smaller amount was continued, however, in order to avoid having the patient depend upon the drug too much, seven and one-half grains being given at 8:00 p.m.

December 24, 1931.

After a night of sound sleep, the patient passed a comfortable day. During the ten days before this date the patient several times volunteered the information that he did not think about morphine. This statement is probably true despite the untrustworthiness of this type of person, because he was in no particular hurry to leave the hospital, and was not in need of any drug. So far as could be determined, the patient had no desire for drugs.

The patient was discharged from the hospital on this date. After being told how much sodium rhodanate had been given to him at different times during two weeks previous to this, he was instructed to administer to himself the quantity that would be effective in all times of stress. Arrangements were made for a periodic check-up on the condition of the patient. Lack of funds made it impossible to hospitalize him for a longer period of time; this would have been very desirable.

January 4, 1932.

It was learned that the patient would not be able to take a position for quite a while because it was necessary for him to be constantly with his aged, infirm mother. The task was arduous in the extreme for a man in his condition. At night, when his mother did not need him, he slept within two feet of a stove, in order to keep the fire burning. At this time the patient was instructed to take five grains of sodium rhodanate and fifteen grains of sodium bromide, a poorer peptizing agent, each night. The feeling of weakness, of which the patient formerly complained, was gone.

January 8, 1932.

The sodium bromide proved not to be efficient enough to give the patient his sleep and allay all nervousness. So, five grains of sodium rhodanate at 4:00 p.m. and ten grains at 9:00 p.m. daily were ordered. The patient was gaining weight slowly at this time. His problems at home were becoming more acute.

January 16, 1932.

The patient was doing well despite the strain that he was under at home. He was told to take sodium rhodanate as needed, in an effort to reduce the amount to a minimum.

February 9, to February 21, 1932.

About this time it was noticed that the facial expression of the patient was not very frank. Further, rumors came from many sources that the patient was using morphine again. Then a packed committee of local doctors vouchsafed unscientific, baseless information to the effect that the patient was not only taking morphine, but was never entirely withdrawn while in the hospital. In the better judgment of more qualified people, this information was incorrect. The circumstances surrounding the treatment of the patient in the hospital made it quite certain that morphine was completely withdrawn. Upon being questioned, the patient named an unscrupulous physician who had supplied him with several grains of morphine with the knowledge that he (the patient) had been treated with sodium rhodanate. It was found that the patient had also secured some pantopon, which is habit-forming.¹

He used the morphine and pantopon for a period of about four days as a result of five successive sleepless nights, which were brought about by the necessity of caring constantly for his mother. Then, struck by remorse, the patient withdrew the morphine in his own home without anyone knowing that he was either using the drug or going through withdrawal. To do this he used large doses of sodium rhodanate; it was not possible to learn the size of the doses of sodium rhodanate that he used. The patient said that he suffered slight withdrawal symptoms during one night. He also said that the first of the one-quarter grain doses of morphine that he used stimulated him much more than that-sized dose ordinarily would. Sodium rhodanate, by its pep-tizing action, must have prevented the morphine from exerting its full ag-glomerating action.

While there was every reason to believe that the above chain of events was substantially correct, scientific proof that the patient was not still taking the drug was desirable. To that end, arrangements were made to have the patient spend several days in the Strong Memorial Hospital² of the University of Rochester under close observation, under morphine-tight conditions. The room occupied by the patient was kept locked; all of his possessions except a toothbrush were taken from him before entering the room; cigarettes were furnished by Dr. McCann; the required clothing, handkerchiefs, toilet articles, etc. were furnished by the hospital. The food on his tray was inspected by the nurse in charge at every meal time. No visitors were allowed. The patient was not given toilet privileges. In other words, everything that could be done, was done to prevent the patient from access to morphine. The patient was admitted to the Strong Memorial Hospital on February 21, 1932. Nothing abnormal was found in the behavior of the patient on that day.

February 22, 1932.

Dr. McCann's report says: "In a short interview, I (Dr. Akelaitis) could find no symptoms of withdrawal. Patient was composed, there was no de-

¹ Kunkel: Clifton Med. Bull., 18, 6 (1932).

² Professor William S. McCann, of the University of Rochester Medical School kindly conducted this experiment and made available a report of the results, thereby adding very valuable data to this study.

pression or psychomotor retardation, no sudorrhea, and no tremor. He talked spontaneously, relevantly, and coherently. No preoccupations or distortions of content. Patient was well oriented, memory for remote and recent events apparently good. Patient is very enthusiastic about sodium rhodanate treatment.

"Dr. Goldstein and I (Dr. McCann) had a long interview with the patient. No symptoms of withdrawal can be detected as yet, and I believe the drug has been pretty well excluded."

February 23, 1932.

No withdrawal symptoms were detected.

February 24, 1932.

"I (Dr. McCann) can see no evidence of withdrawal symptoms. I do not think that there has been any leak in our system of excluding morphine.

February 25, 1932.

"Behavior most exemplary. No signs of withdrawal or of morphine. Pupils medium size. No lachrymation, salivation, or any evidence of distress."

February 26, 1932.

No evidence of withdrawal symptoms was seen. "The measures which we have used to exclude his access to morphine have been very rigid, and included digital examination of the rectum and daily enemas. It is my (Dr. McCann's) opinion that he has had no morphine during his stay here of five days and that no symptoms of withdrawal have been noted.

"The patient made several interesting statements. He said that sodium rhodanate did not entirely alleviate his suffering during the withdrawal experiments at Ithaca. He was so ill at one time that he received enough anytal to produce a stuporous condition.

"Since the 'cure' he admits having received several quarter grain doses of morphine and some 'pantopon' tablets. His comment on this is as follows: 'That ordinarily these small relapses would have brought back immediately all of his former terrible cravings.' He attributes the fact that this did not occur to his continued use of sodium rhodanate."

February 26, 1932.

No symptoms of withdrawal were observed on this day. The patient told Dr. McCann that his period of illness during withdrawal under sodium rhodanate was part of one day; whereas, it was always of three or four days duration on previous withdrawals. "He feels that he was benefited definitely by the rhodanate."

When the patient was left at the Strong Memorial Hospital, he was instructed to tell the doctors there nothing but the truth, even if it did not agree with what he had told us.

From this there seems to be no doubt but that the patient withdrew himself at home after using morphine for several days. It was an experiment that

we would have liked to have tried but would not have dared to. Such an experiment as this should prove beyond a question of doubt that sodium rhodanate is beneficial in the treatment of drug addiction.

February 29, 1932.

The patient was gaining weight rapidly at this time. He appeared to be quiet and on an even keel.

March 18, 1932.

This day provided another interesting study of the patient. He came to us in the worst hypomanic condition in which we had ever observed him. He had been drinking whiskey all of the week. Investigation revealed that he had not had any sodium rhodanate during the week previous to that of March 18. He was dirty, disheveled, and intoxicated; his speech was not well coordinated. He was oblivious to those around him; his face was gray, and exhibited nervous tension. He claimed to have used a quart of whiskey during the day. The patient was thoroughly disgusted with himself.

Twenty grains of sodium rhodanate were administered at 9:30 p.m.; at this time he was also given "Bisodol" and psychotherapy without hypnosis. By 10:00 p.m. he was out of the hypomanic state, and much quieter. Ten grains more of sodium rhodanate were given at this hour. The grayness and lines soon left his face; he became more quiet; and by 10:30 he was completely sober; he talked and acted sober, in every respect. "Bisodol" was administered again at this time. The sight of whiskey sickened him so that he vomited. He returned home sober with instructions to take ten grains more of sodium rhodanate before retiring. He slept well during the night.

It was not difficult to see that the patient could not be trusted to administer sodium rhodanate to himself only when needed. When he did not need it, he would not take it. This generally resulted in sleeplessness, nervousness, and a return to the hypomanic condition. He would then use sodium rhodanate in too large quantities. This upset him on the over-dispersion side. Except for the intervals in between, the patient was feeling upset. As a result he went on an alcoholic spree.

March 25, 1932.

The patient was quiet and in excellent condition, when seen on this date.

March 30, 1932.

At this time the patient was in one of his quiet intervals after having used too much sodium rhodanate. He was in good condition, quiet, and relaxed. He said that he had not felt better in years; the pupils of his eyes were normal in size. He claimed that he never thinks of morphine; he was sleeping about ten hours each night.

In order to try to keep him on an even keel two sets of capsules were made up for him. One of them contained ten grains of sodium rhodanate with one-quarter of a grain of saccharin to act as a disguise. The other contained one grain of ephedrine sulphate, and ten grains of sodium bicarbonate. The

sodium bicarbonate was to keep his stomach settled; and the ephedrine to keep the blood pressure up, and as an added peptizing agent. One capsule of each was to be taken every other night.

April 1, 1932.

The ephedrine, in addition to the psychic effect of a change to an unknown medicine, brought about a slight sympathetic nervous upset. The patient refused to use the capsules, and requested sodium rhodanate. He was quiet and fairly well relaxed when seen on this date.

April 6, 1932.

The patient was intoxicated again. Sodium rhodanate was administered; and it straightened him out within two hours. The twofold problem then presented itself. In the first place, the patient had learned from experience that he could use either morphine or alcohol for short periods of time and rely upon sodium rhodanate to stop their use. Secondly, it was difficult to make him use a constant small amount of the peptizing agent. At this time he was instructed to take ten grains of sodium rhodanate every night, with the hope that he would do so.

April 19, 1932.

The patient was looking and feeling very well on this date. Evidently he had been using the sodium rhodanate as he was instructed.

April 23, 1932.

When seen, the patient was in a hypomanic condition. Still, he was feeling well. He had gained quite a bit of weight.

From various sources, it was learned that during previous withdrawals the patient was: ill for three or four days, depressed, cranky, "a mean customer," whiney, paranoid, subject to severe gastro-intestinal upset, with cramps, diarrhea and nausea, bothered by hot and cold flashes, tremors, inability to satisfy his craving for food, twitches, profuse perspiration, yawning, a craving for the drugs, sneezing, and a crawling sensation in the lower abdomen. His bones and joints ached; he was restless. One doctor said that the patient suffered severely all of the common withdrawal symptoms, and was a "mean customer."

In contrast with this, it was found that under the sodium rhodanate treatment the patient exhibited a slight gastro-intestinal upset of short duration, short periods of yawning, a very little muscular aching for a few hours, and restlessness. There was delirium, which has not been reported as being a factor in other withdrawals that the patient went through.

A good many data of a physical nature have been accumulated during the study of this case. It is of advantage to present it here. Table II gives the variations in blood pressure and weight of the patient from the start of the experiment. The data show that the blood pressure at the start of the experiment was low, as is common with drug addicts. During the whole time that the patient was under treatment the systolic pressure rose slightly. The

definite upward trend did not begin until nearly the end of the withdrawal period. The statement is made in the report of Lambert's committee, p. 490, that there is often a fall in the systolic and diastolic readings during withdrawal. The opposite was found here. The diastolic readings did not vary much at any time; although there was a slight upward trend during withdrawal. These blood pressure data do not bring to light any vasomotor instability.

TABLE II

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
12- 1-31	115/70	—	12-14-31	—	135
12- 2-31	105/65	139	12-15-31	—	135½
12- 3-31	120/70	140	12-16-31	122/70	—
12- 4-31	112/60	141	12-17-31	122/75	140
12- 5-31	115/70	141	12-18-31	—	140
12- 6-31	113/68	142	12-22-31	105/70	—
12- 7-31	115/68	141	12-23-31	—	140¾
12- 8-31	122/68	138	1-16-32	—	153
12- 9-31	120/74	139	2- 9-32	—	149½
12-10-31	130/75	139	2-21-32	120/75	—
12-11-31	135/78	135½	2-29-32	—	157½
12-12-31	135/74	135	4-23-32	140/85	164
12-13-31	—	135			

The changes in weight that the patient underwent are of interest. During the early part of the withdrawal he gained weight. He did not lose weight until two days after withdrawal. This can be attributed to the six bowel movements on December 10, in addition to the fact that his appetite was not hearty from the eighth to the twelfth of December. After the withdrawal, the patient did not gain weight rapidly, as is usually the case. This is ample proof of the absence of severe withdrawal symptoms, in the first place, and the non-appearance of the "chuck horrors," in the second place.

Table III shows the volume of the urine for twenty-four hour periods during hospitalization. While there was not a constant water intake during the study, the general trend of the output figures is of great interest. The initial increase in the volume may be due to a decrease in the amount of water adsorbed by the blood serum and nervous system proteins. Morphine is carried to the liver or intestines by the blood for destruction or elimination. The peptizing action of the rhodanate ion throws morphine off of the particles on which it is adsorbed. This will tend to increase the amount of free morphine in the body fluids. If, then, this available morphine goes to tissues that have not taken up much of it before, and have not taken up much sodium rhodanate, dehydration will take place. This, in turn, may increase the water output.

TABLE III

Date	Volume in Ounces	Date	Volume in Ounces
12-3-31	46	12- 9-31	17
12-4-31	51	12-10-31	15
12-5-31	58	12-12-31	15
12-6-31	30	12-14-31	30
12-7-31	80	12-22-31	30
12-8-31	30		

The sharp decrease in water output (the values are well below the average)¹ from the ninth to the twelfth of December inclusive is interpreted as being due to adsorption of water by the colloids of the body that were then being peptized by the rhodanate ion. From the fact that a large decrease in water output occurred on the next day after the patient was given his last dose of morphine, one can surmise that the sodium rhodanate was forcing the morphine out of the system at greater than the normal rate. Other evidence will be cited which sustains this view.

The phenolsulphonephthalein test for kidney function² was performed on the patient at intervals. The results are given in Table IV.

TABLE IV

Date	cc. Urine First Hour	cc. Urine Second Hour	% of Dye Eliminated First Hour	% of Dye Eliminated Second Hour	% of Dye Total
12- 1-31	240	100	72	21	93
12- 7-31	65	115	18	5	23
12- 8-31	90	20	71	2	73
12- 9-31	95	65	72	18	90
12-11-31	128	30	76	14	90

The data show that the patient had a high renal function at the start of the experiment. The function became very poor, and then recovered. The dye was injected intravenously; this brings up the possibility that the low function found on December 7, may have been due to the transfixation of the vein. However, the kidney function was lower than would be expected on the next day. That 23% was a real value is supported by data obtained on another case. Were the kidneys adsorbing large amounts of morphine at this time?

Table V is given merely to show that the patient did not exhibit any upset that can be gauged by changes in rate of pulse or respiration.

¹ Starling: "Principles of Human Physiology," 893 (1930).

² Hawk and Bergeim: "Practical Physiological Chemistry," 675 (1926).

TABLE V

Date	Rate Pulse	Rate of Respiration	Date	Rate Pulse	Rate of Respiration
11-30-31	70	22	12-13-31	80 88	20 20
12- 1-31	70 70	22 20	12-14-31	70 70	20 20
12- 2-31	72 76	20 20	12-15-31	72 70	20 18
12- 3-31	68 60	20 20	12-16-31	72 72	18 18
12- 4-31	70 62	18 18	12-17-31	70 88	20 20
12- 5-31	60 60	20 20	12-18-31	92 92	20 20
12- 6-31	68 70	22 20	12-19-31	90 80	20 20
12- 7-31	72 70	20 20	12-20-31	70 80	18 18
12- 8-31	72 72	20 22	12-21-31	76 80	20 20
12- 9-31	70 74	22 20	12-22-31	72 84	18 20
12-10-31	72 70	20 20	12-23-31	90 80	22 20
12-11-31	92 78	30 32	12-24-31	76 80	20 22
12-12-31	70 68	18 18	2-21-32	84	20

Through the kind cooperation of the Tompkins County Laboratory, the data in Table VI were secured. The values for the 22d of February were taken from the report of Dr. McCann. The data show that until nearly the end of the withdrawal period the patient had a relative lymphocytosis. After withdrawal the basophiles and eosinophiles dropped out of the picture largely;

and the condition became one of polymorphonuclear leucocytosis. The leucocytosis which developed upon withdrawal is generally encountered in this type of case.¹ This leucocytosis began to subside; and the original lymphocytosis reappeared. When the number of white blood cells increased again, the percentage of polymorphonuclear leucocytes increased more than the percentage of lymphocytes. Since Takacs² showed that sodium rhodanate may produce a leucocytosis, it seems a fair assumption that the second rise in the number of white blood cells was due to that drug. The final blood count was normal. Throughout the study, the monocytes were somewhat below normal in percentage.³

TABLE VI
Hematology

Date	W.B.C.	Polys.	Lymps.	Monos.	Eosins.	Basos.
12- 1-3 I	7,850	66 0%	30.5%	1.0%	2.0%	0.5%
12- 2-3 I	9,750	64.5%	29.5%	2.0%	3.0%	I
12- 3-3 I	10,300	73 5%	23 5%	0.5%	2.0%	0.5%
12- 4-3 I	8,525	61.5%	34 5%	0.5%	2.0%	1.5%
12- 5-3 I	9,000	64.0%	33.0%	2.0%	0	1 0%
12- 7-3 I	10,600	66.0%	31.5%	1.0%	1.0%	0 5%
12- 8-3 I	13,200	77.0%	20.0%	3.0%	0	0
12- 9-3 I	14,600	73 5%	24 5%	1.5%	0	0.5%
12-10-3 I	14,000	77.5%	20.0%	2 0%	0	0.5%
12-11-3 I	11,550	74.5%	23.5%	2.0%	0	0
12-12-3 I	10,000	62 0%	36.0%	2.0%	0	0
12-14-3 I	11,300	69 0%	29 0%	2.0%	0	0
12-15-3 I	13,000	74 5%	23.0%	2.0%	0	0.5%
12-16-3 I	14,250	76 0%	22.0%	2.0%	0	0
12-17-3 I	16,550	80 0%	18.0%	1.0%	1 0%	0
12-18-3 I	14,475	78.5%	19.0%	1.0%	1.0%	0
12-19-3 I	16,800	77.5%	21.5%	0.5%	0 5%	0
12-21-3 I	11,300	76 0%	22.0%	1.0%	1.0%	0
12-23-3 I	13,250	77 0%	21.0%	2.0%	0	0
2-22-32	8,200	75.0%	20.0%	—	—	1.0%

Routine urinalyses were made almost every day while the patient was confined to the hospital. The data are given in Table VII. There was a definite increase after an initial decrease in specific gravity with the progression of time; the higher figures are somewhat above normal. In all probability, this is due to the presence of **sodium rhodanate**, which is eliminated by the kidneys. An added factor is that sodium rhodanate doubtless forces sodium chloride out of the body, because the rhodanate ion is more strongly adsorbed by the proteins than the chloride ion. No sugar was found in the urine at any time during the study.

¹ Lambert et al: *Am. J. Psychiatry*, 10, 433 (1930).

² *Z. ges. expt. Med.*, 50, 430 (1926).

³ Starling: "Principles of Human Physiology," 657 (1930).

TABLE VII

Date	Appearance	Reaction	Sp. Grav.	Albumin
12- 1-31	Cloudy amber	Alkaline	1.025	Trace
12- 3-31	Clear straw	Acid	1.021	"
12- 4-31	Cloudy straw	Acid	1.021	"
12- 5-31	Cloudy straw	Acid	1.016	"
12- 6-31	Cloudy amber	Acid	1.025	—
12- 7-31	Cloudy amber	Acid	1.027	Trace
12- 8-31	Cloudy amber	Alkaline	1.019	"
12- 9-31	Cloudy amber	Alkaline	1.031	"
12-10-31	Cloudy amber	Alkaline	1.032	"
12-12-31	Cloudy amber	Acid	1.035	"
12-14-31	Cloudy straw	Alkaline	1.030	"
12-15-31	Clear amber	Alkaline	1.031	"
12-17-31	Clear amber	Neutral	1.030	Ft. Trace
12-18-31	Clear	Acid	1.030	Ft. Trace
12-19-31	Straw	Alkaline	1.030	Ft. Trace
12-21-31	Clear amber	Acid	1.036	Trace
12-22-31	Cloudy straw	Alkaline	1.036	Ft. Trace
12-23-31	Cloudy amber	Alkaline	1.031	Ft. Trace
2-22-32	Clear amber	Acid	1.034	None

It is interesting to note that the urine became alkaline toward the end of the withdrawal period. If there was a true alkalosis, it undoubtedly played a useful part in the peptization therapy; because the hydroxyl ion is even a better peptizing agent than the rhodanate ion. This does not mean in any way that the rhodanate ion was not responsible largely for the suppression of the abstinence symptoms. The data show that sodium rhodanate did not bring about a condition of albuminuria. This negative finding is of value only as it points out the safety of sodium rhodanate in this respect when used in large doses.

Table VIII shows the variations in basal metabolic rate at intervals during the course of the treatment. The data show that the patient's basal metabolism was within the normal limits of plus or minus ten percent. On the eighth of December, when the dosage of morphine was very low, the basal metabolic rate was low. If there was much nervousness, one would expect the metabolic rate to be higher, barring complicating factors. Thus, yet another physical test demonstrates that the patient was not greatly upset during withdrawal. The data also show that sodium rhodanate, in large doses, does not affect the thyroid gland.

TABLE VIII¹

Date	Metabolic Rate	Date	Metabolic Rate
12-2-31	+ 1%	12-12-31	+8%
12-5-31	- 10%	12-19-31	+3%
12-8-31	- 1%		

¹ The staff of the Tompkins County Laboratory kindly secured these data.

Tests of the rate of sedimentation of the red blood corpuscles, using citrated venous blood, showed a high rate which exhibited no definite trends, one way or another. Experiments showed that, by adding sodium rhodanate to the blood samples, the sedimentation rate of the red cells can be decreased tremendously.

Two psychological tests were performed at frequent intervals during the treatment. The first was a dictation-writing test, in which an eighty-four word section of an article was read to the patient, a phrase at a time. The patient was required to take down the dictation as rapidly as he could. The time to accomplish this was recorded. The test was performed at the same time each day; this rules out the factor of the relationship between the times that morphine was given and the test was made. According to Dr. Lang¹ this provides a measure of the involvement of the hearing and the projection system from the ear, to the writing center, to the hand. In Table IX the data obtained on giving this test are set down. The data show that the patient was not seriously upset until December 7th, and that he made a rapid recovery.

TABLE IX

Date	Number of Words	Time needed	Number of Mistakes	Remarks
12- 3-31	84	5 min. 45 8 sec.	2	
12- 4-31	84	3 " 48 0 "	1	
12- 4-31	84	2 " 52.2 "	1	Well person, same dictation, writing illegible.
	84	3 " 0.0 "	1	Well person.
12- 5-31	84	3 " 41 6 "	1	Writing less legible.
12- 6-31	84	3 " 14 2 "	0	Writing more compact and legible.
12- 7-31	84	3 " 40 6 "	6	Writing poor.
12- 8-31	84			Delirium, no test.
12- 9-31	84			No test. Delirium on awakening.
12-10-31	84	3 " 49 4 "	3	Handwriting not steady.
12-22-31	84	4 " 1 8 "	1	Handwriting better than at start.

The other test, which was performed until the last day that the patient was given morphine, consisted of crossing out the letter "O" whenever it occurred in a given paragraph. The paragraph was different each day; but it was from the same magazine, so that the letters were all in the same size type. The patient was timed with a stop-watch while performing the task. The number of "O's" that he crossed out divided by the total number in the paragraph was taken as the accuracy. The data that were obtained are given in Table X. The test was performed just before the preceding one each day. It appears from this that there was no serious fatigue or attention defect until the final day of withdrawal. On the 9th of December this test, and the preceding one, were attempted just as the patient was awakening. At such times during that day, the patient was irrational.

¹ Private Communication.

TABLE X

Date	Number of O's	Time required	Number missed	Accuracy
12-3-31	44	1 min. 12.4 sec.	7	84.1 %
12-4-31	41	1 " 26.2 "	4	90.25%
12-5-31	41	1 " 5.2 "	2	95.1 %
12-6-31	41	1 " 9.0 "	4	90.25%
12-7-31	43	1 " 41.0 "	3	93.1 %
12-8-31	Test not done.			
12-9-31	Patient could not do test.			
Normal Subjects	41	1 " 22.8 "	2	95.1 %
	32	43.2 "	0	100. %
	48	1 " 6.8 "	1	97.9 %
	41	51.0 "	0	100. %

By comparison with the few controls that are given at the bottom of Table X, the patient was somewhat slow and inaccurate in performing this task. This test did not bring the nervousness of the patient to light, as the dictation test did.

Since this patient shows evidences of a manic-depressive psychosis, he should not return to the habitual use of morphine, if he will consistently take sodium rhodanate for a period of months. The peptizing action of the rhodanate ion should relieve him of the hypomania, nervousness, and sleeplessness, and thus perhaps counteract an inadequate personality. When the administration of the medicine was supervised, it was observed to accomplish these ends.

Case 2, H. A.

The patient was a white male, aged 48, who had been taking four grains of morphine sulphate per day for not less than two years. He was admitted to the hospital on the 18th of January, 1932. No attempt was made to study him during that evening. The same precautions were taken to exclude morphine as were followed in Case 1.

A physical examination revealed that with a few exceptions the patient was normal. The knee jerks were equal but hyperactive. His weight was well maintained. His expression revealed some nervousness and tenseness; there was a definite substratum of apprehension. His skin was dry.

A general survey of the patient left the impression that he was very jealous of his own comfort, and extremely impatient. On a careful observation, one could detect delusions of grandeur. Further investigation revealed the fact that for years he had had hypochondriacal tendencies. This was his first experience in the withdrawal of morphine; he was a man of good standing in his community. The patient, while not psychotic, tended toward hypomania; he was a salesman. He claimed that morphine depressed him.

Table XI shows how the dosage of morphine was reduced, and the amounts of sodium rhodanate that were given during the withdrawal period. The data in this table play an important rôle in the elucidation of some of the later events.

TABLE XI

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-19-32	4	0.00	1-23-32	5/8	4.00
1-20-32	3½	1.00	1-24-32	0	0.00
1-21-32	2	2.33	1-25-32	0	0.33
1-22-32	1	3.33	1-26-32	0	0.67

January 19, 1932.

During the night the patient had a chill which lasted but a few seconds. After sleeping poorly, he awoke in an irritable frame of mind. He had a low fever, and was somewhat delirious. In the morning he refused a bath and refused nourishment. Throughout the morning the patient complained of feeling chilly. At 10:00 a.m. he complained that he ached all over his body.

At noon he had worked up a fever of 102°F. Upon examination his chest was normal. He was somewhat apprehensive during the day. These observations are given in order to demonstrate the great degree of suggestibility, and impatience of the patient. Nothing more was seen of the chill reaction. He was nervous and restless when the administration of morphine was delayed for one hour, in the evening.

January 20, 1932.

The patient slept better during the night than he had through the previous night. He was nervous and irritable when he awoke, although he was brighter than he had been. The administration of morphine was regulated so that it was given at 6 a.m., 11 a.m., 4 p.m., and 10 p.m. He was irritable and restless when he was taken to the basal metabolism room instead of being given his breakfast. The basal metabolic rate was +13%. Like many morphine addicts, the patient smoked incessantly. In the evening he became restless and irritable again; but, on the whole, the patient passed an easier day. Fifteen grains of sodium rhodanate were given at 11:00 p.m.

January 21, 1931.

During the night, the patient slept more soundly and longer than he had in years. He was given eight ounces of magnesium citrate solution at 6:00 a.m. An hour later ten grains of sodium rhodanate were administered. Slight nervousness and yawning were observed during the morning; the patient was comfortable, nevertheless. The pupils of the eyes were not so contracted as they had been. It was obvious that he was used to being waited upon, and expected it. Five grains of sodium rhodanate were given at 11:00 a.m.

Except for some nervousness and excitement at 3:30 p.m., one-half hour before his dose of morphine was due, the day was uneventful. During the early evening the patient slept at intervals. From 9:00 until 10:00 p.m. he was slightly nervous. At 11:00 p.m. fifteen grains of sodium rhodanate were administered; fifteen minutes later the patient was sleeping soundly.

January 22, 1932.

At 2:10 a.m. the patient awoke, and complained of feeling chilly and of a pain in his abdomen. His skin was covered with perspiration. Ten grains of sodium rhodanate were given at 2:30 a.m. to combat these symptoms. At 2:40 a.m. the patient was sleeping soundly. He passed a comfortable night. Five grains of sodium rhodanate were given at 8:00 a.m., at which time the patient was irritable, and refused to have a basal metabolism test.

Relatives of the patient gave out the information that he always had to be humored even during very minor physical upsets; at the least sign of a physical disturbance he was prone to consult a doctor. The patient said that care must be taken that he should not vomit during the withdrawal; for it would be impossible to stop if it once got started.

In the fore-noon the patient said that he ached slightly all over, the most pronounced ache was in the back. The pupils of his eyes were dilated somewhat, for a brief period around ten o'clock. At noon he said that he felt badly all over; he smiled broadly as he made this statement. There was not a great deal of hyper-motor activity. The patient claimed that he could feel distinctly the quieting effect of sodium rhodanate.

At noon five grains of sodium rhodanate were administered. The patient slept from one until two o'clock. Several times during the afternoon he complained of pains in the legs, back, and neck. Five grains of sodium rhodanate were given at 5:00 p.m. The impression was that any suffering that there was, was largely mental.

The patient was restless and irritable during the evening. To combat this ten grains of sodium rhodanate were used at 8:10 p.m. At eleven o'clock the patient was given fifteen grains of sodium rhodanate; he slept from that time until 2:20 a.m.

January 23, 1932.

At 2:30 a.m. the patient awoke, and complained of feeling cold. When given sodium rhodanate (five grains) he vomited immediately. The patient then proceeded to try to make good on his prediction that there would be trouble should he start vomiting. Amidst a good deal of hyper-motor activity which resulted in various gyrations he tried to vomit without result. These antics lasted for about one-half hour, following which one-eighth of a grain of morphine at 3:10 a.m. quieted him somewhat. At this time he refused sodium rhodanate, claiming that it made him sick. During the early hours of the morning, he was rather disconsolate. He talked constantly and loudly; he did not complain of pain. The patient was quite determined to have his own way. Fifteen grains of sodium rhodanate were administered at 6:30 a.m.; he became quieter then. The patient's appetite for breakfast was very poor.

At eight o'clock he complained of pain in the back, legs, and back of the neck. There was no evidence of suffering. At times he felt nauseated. The patient slept at intervals throughout the morning. Eight ounces of magnesium citrate were given at 11:30 a.m. When sterile hypodermic injections were made at the hours that morphine was due, a little novocaine was dissolved in

the water. Fifteen grains of sodium rhodanate were given at 12:30 p.m.; at the same time ten grains of sodium bicarbonate were administered in order that the sodium rhodanate should not upset the stomach so much. His appetite was poor at noon.

During this day, and the day before, the patient smoked less than he did previously. In each one of these cases it has been noticed that the patients smoke progressively less for a period of about two weeks. There are considered to be two factors involved in this. In the first place the sodium rhodanate quite evidently makes the cigarette smoke taste bad. Secondly the patients become less nervous, except for about a day, which brings about a reduction in the amount of smoking.

Between one and two o'clock the patient was very irritable and restless; there was a good deal of hyper-motor activity. The last administration of sodium rhodanate, when viewed in retrospect, appeared to excite him somewhat. He walked madly up and down the corridor, refused to listen to reason, and declared that he wanted either to die or continue taking morphine. He said that the treatment was not helping him. Careful observation by several people failed to detect any signs of physical suffering; at no time, from this date on, was physical suffering a part of the picture, so far as could be determined. On the other hand, there is no question but that he was mixed up mentally to quite a considerable extent.

The patient's back was rubbed for one-half hour between 2:00 and 2:30 p.m. This quieted him so that he dozed for about one-half hour. Had there been much physical distress, that effect probably would not have been produced. At 3:30 p.m. fifteen grains of sodium rhodanate were given. This precipitated delirium within an hour; the patient became very restless and nervous. At times he screamed, largely to attract attention to himself. He threw himself around, and refused to stay in bed.

Between six o'clock and midnight he vomited yellow fluid four times. The patient was not maniacal or hard to restrain; he became quiet when spoken to authoritatively. At the same time he attempted to demonstrate that he was uncontrollable, which was not the case. At 6:00 p.m., and again at 7:20 p.m., he was given one-eighth of a grain of morphine. The quieting effect was noticed. At 10:30 p.m. ten grains of sodium rhodanate were given. The delirious condition lasted throughout the night.

January 24, 1932.

Two compound cathartic pills were administered at 12:30 a.m., immediately following which the patient had a liquid bowel movement. Later in the morning, there was another liquid bowel movement. During the early morning, the patient was very noisy. Twice he complained of tenderness in the abdomen. At 5:00 a.m. tetanic twitches began, and became pronounced. This phenomenon has been explained already. It is worthy of note that none of the patients treated by sodium rhodanate were bothered by the twitches; none of them ever complained about it. He vomited again at 8:00 a.m.

Except at short intervals, the patient was not rational all day long. From noon until two o'clock he slept in very short naps. After that, until seven

o'clock, he became progressively quieter. Several times during the day and evening he told those attending him to leave him alone, and not bother him. From 9:00 p.m. until 10:00 p.m. and from 11:00 p.m. until midnight the patient slept at short intervals. These periods were interspersed with periods of restlessness. During the evening he was more rational than he had been. No sodium rhodanate was administered during the twenty-four hour period.

January 25, 1932.

During the early morning, the patient slept for four hours. He was less irrational and restless than he had been. He vomited again at 8:30 a.m., and then slept soundly for an hour. After being more or less irrational all morning, he quieted down and cleared at about 2:00 p.m. The patient was rather quiet all afternoon.

The patient was given five grains of sodium rhodanate at 8:10 p.m. He was restless after that, and complained that he was very ill and going to die. He jumped up and down, and moved about a great deal in the bed. He was disagreeable; in a half-hearted attempt to find his way out, he ran up the hallway. Except for brief intervals, the patient was irrational all night long. It should be emphasized again that no physical suffering was observed by those attending the patient. Twice before midnight he asked for morphine. He and one other patient were the only ones who asked for morphine after the withdrawal.

January 26, 1932.

He did not sleep much during the night; he was very restless, and at times disagreeable. The delirium persisted. Around eight o'clock in the morning the patient became rational. During the rest of the morning he was quieter than he had been. He continued to be quiet all afternoon. He was given five grains of sodium rhodanate at 12:40 p.m.

In the afternoon the patient complained of feeling weak all over. All of the patients that have been treated by this method have complained of feeling weak. This is not due to loss of weight, lack of nourishment, or lowering of the blood pressure; because there generally has not been an excessive loss of weight, lack of nourishment, or drop in blood pressure. It may be due to a rapid reversal of the colloids of the nervous system.

At 10:00 p.m. the patient was given five grains of sodium rhodanate. He passed a quiet night.

January 27, 1932.

The patient slept practically all night long. In the morning he said that he did not care to talk because he had had a nervous disease. He was given five grains of sodium rhodanate at 7:00 a.m. and again at 2:00 p.m., and ten grains at 10:00 p.m.

Aside from short periods of restlessness, nervousness, and forgetfulness the day and evening were uneventful. His appetite was good.

January 28, 1932.

There was no lack of sleep during the night. The patient complained of aching legs at 6:00 a.m., and asked for sodium rhodanate ahead of time.

Five grains were given. His appetite continued to improve. Five grains of sodium rhodanate were given at 2:00 p.m. He was slightly nervous and restless at times during the day. Physiotherapy was employed to combat the ache in the legs of which he complained. For three days, despite the report of nervousness, the patient was able to hold his arm and hand extended with less tremor than could those attending him.

Fifteen grains of sodium rhodanate were given at 10:00 p.m. There followed six hours of practically uninterrupted sleep.

Thus, nine days after entering the hospital the patient appeared to be in pretty good condition. The mental reaction to the withdrawal was more severe than in Case 1; but the physical symptoms were no more marked, despite the fact that this patient was less stoical than Case 1. It seems evident that he was withdrawn somewhat too rapidly for the maximum ease. Perhaps the delirium, in this case particularly, can be regarded as an expression of the irritability through which living tissue goes upon agglomeration, and again upon return to normal. Since the rhodanate ion probably forces the morphine off of the tissues more rapidly than it would come off in gradual withdrawal alone; an accentuated irritability might result. Much the same thing has been observed with rabbits in their reactions to sodium amytal and ether.¹ The rabbits were much more intoxicated when forced rapidly out of the anesthesia by sodium rhodanate.

January 29, 1932.

After passing a comfortable night, the patient complained of a backache. He was uneasy and his appetite was poor. Five grains of sodium rhodanate were given at 7:00 a.m.

At this point, the reactions of the patient again assume real importance; for later events showed that he was forced into a psychosis as a result of over-dispersion with sodium rhodanate. At 10:00 a.m. he expressed dissatisfaction with hospital life. Five grains of sodium rhodanate were given at 2:00 p.m. Shortly thereafter he became very nervous.

In the evening his appetite was good. Later he became restless and manifested constant motor activity. Five grains of sodium rhodanate were given at 10:00 p.m. He slept for about seven hours thereafter. He cried out in his sleep once.

January 30, 1932.

Upon awakening in the morning the patient was very nervous. Five grains of sodium rhodanate were given at 7:00 a.m. He was restless during the morning. At 2:00 p.m. he was given ten grains of sodium rhodanate. While playing cards in the afternoon he did not bother to wait for the opponents to put their cards on the tricks.

In the evening at eight o'clock fifteen grains of sodium rhodanate were administered. Constant motor activity followed. He became more nervous and talked irrationally at times.

¹ Bancroft and Rutzler: *J. Phys. Chem.*, **35**, 1185 (1931).

January 31, 1932.

He slept at intervals during the night, and cried out several times. During the early morning hours he was irrational most of the time. Ten grains of sodium rhodanate were administered at 7:00 a.m. In the forenoon he was nervous, irrational, and manifested constant motor activity. He complained that he was not being given any medication; he refused to eat dinner until sodium rhodanate was administered. He was given seven grains of the medicine at noon; after which he ate well. Ten grains of sodium rhodanate were given at 2:00 p.m.

In the evening the patient seemed quite confused at times; he was very nervous, talked incoherently, and forgot where his room was. At 8:00 p.m. fifteen grains of sodium rhodanate were given. Illusional episodes were observed, in that he heard low voices speaking in another room to someone else and thought that he was being addressed.

February 1, 1932.

The patient fell out of bed at 12:30 a.m. without being injured. The constant motor activity was in evidence at 1:00 a.m.; he was unable to answer questions coherently. Later in the morning he became noisy. He did not sleep much during the night. Throughout the morning the patient was irrational. He asked for sodium rhodanate frequently. Systematized delusions of persecution appeared. He talked about signing papers and about different people coming to see him. After becoming more irrational as the morning progressed, the patient jumped out of a window, despite a snow storm, clad only in his pajamas and a bathrobe. He ran into the entrance of the hospital, some eighty yards distant, calling for the police. He said that he came back into the hospital because he knew that he would be caught. The patient continued to be irrational.

It was realized then that the patient had been over-peptized and that a definite psychosis had developed therefrom. This was not the cause for very much concern because from previous work with functional psychoses¹ the use of an agglomerating agent was indicated. At 12:30 p.m. the patient was given six grains of sodium amytal in capsules by mouth to produce agglomeration. Shortly thereafter he began to scream and to talk constantly. At 3:00 p.m. he was still noisy and restless. At this time he refused sodium amytal claiming that he was being given poison.

Six grains more of sodium amytal were given at 5:00 p.m. This quieted him somewhat; he slept from seven until nine o'clock. The patient was restless and noisy in his sleep after eight o'clock. By 9:20 p.m. he was awake, irrational, and talking constantly. At eleven o'clock he was becoming uncontrollable. Six grains of sodium amytal were given at 11:30 p.m. He went to sleep at midnight.

February 2, 1932.

The patient slept until 2:30 a.m. He then became restless and very noisy. At 2:45 a.m. he was given six grains more of sodium amytal. It is

¹ Lang and Paterson: *J. Phys. Chem.*, **35**, 3425; Bancroft and Rutzler: 3452 (1931).

well to point out here that despite the fact that the sodium amytal did not appear to be helping much, the firm conviction was held that agglomeration was indicated. With that in mind the sodium amytal was continued, and given to effect. At just such a juncture as this one could have fallen down completely by discontinuing the sodium amytal. The theory called for dosage to effect, and that procedure was followed.

The last of the sodium amytal kept the patient asleep until 6:50 a.m. When he began to become restless again, six grains more of the agglomerating agent were administered. Needless to say, fluids were kept up during this time. He was quiet until after 11:00 a.m.; he then became noisy. Three grains of sodium amytal were given at 11:50 a.m. He was restless again at 2:00 p.m.; so three grains more of the drug were administered. This kept him semi-conscious or asleep until midnight. He muttered a great deal during this time.

It took thirty-six grains of sodium amytal to keep the patient asleep for thirty-six hours. That being a rather large amount, would seem to give a quantitative measure of the over-dispersion that was produced by the sodium rhodanate.

February 3, 1932.

At 12:10 a.m. the patient was awake and screaming. Following that he was rational for a short time. He slept at intervals until 7:00 a.m.; another rational spell was observed at 3:10 a.m. The night was less stormy.

During the day the patient was restless at times and rational most of the time. He exhibited the definite delusion that the men attending him were police officers, and that there was a machine gun being aimed at him from the closet.

At noon a switch was made to another agglomerating agent, ipral; three grains were given by mouth. This was repeated at 11:00 p.m. It is interesting to note the paranoid coloring to this psychosis, which was characterized by over-dispersion. That agglomeration of certain centers, and also peptization, perhaps of other centers, gives rise to paranoid symptoms seems evident. Sodium rhodanate produces these symptoms by peptization. Also, morphine produces them by agglomeration. Finally, sodium rhodanate decreases the symptoms of dementia praecox paranoid, an agglomerated condition, but produces much the same symptoms when too much is used. This must mean that paranoid symptoms occur both in over-agglomeration and in over-dispersion. It is probable that cases will be found, which will be classified as dementia praecox paranoia, and which will respond favorably to treatment with sodium amytal.

February 4, 1932.

The patient slept well during the morning hours, and was much more rational at 8:00 a.m. Three grains of ipral were given at 7:45 a.m. and 10:15 p.m.; and one and one-half grains were given at 11:45 a.m.

During the afternoon the delusional field suddenly vanished completely, and the psychosis was at an end. The patient, curiously enough, was able to relate in detail all of his experiences since the last day that he had morphine.

From that point on, the patient improved very rapidly. The course was uneventful. His appetite became very good; his outlook was excellent and he was not nervous. There were no further signs of the psychosis. His irritability disappeared. At bed time on February 5, and 6, he was given one and one-half grains of ipral to ensure his sleeping. The drug was discontinued then. Iron, quinine, and strychnine was administered as a tonic. On February 15, the use of sodium rhodanate was recommenced. Five grains were given each night to help the patient sleep and to combat any nervousness that might arise.

As was usual with the cases reported in this paper, the patient complained of feeling weak. Exercise and food combined to eradicate that difficulty. The extreme jealousy of his own comfort seemed to disappear at least a week before the patient was discharged. All of the nervous tension disappeared from his face; and he was contented to stay in the hospital until told that it was advisable to go home. The patient was discharged on February 20 with instructions to report at times, and to combat any nervousness or sleeplessness by the use of small amounts of sodium rhodanate.

On March 20 the patient was interviewed and found to be in excellent condition physically, and mentally. On April 26 the patient was well, and in a happy frame of mind. There was apparently no need or desire for morphine. He even found that it was not necessary to use sodium rhodanate at that time. On June 18th the patient was well and not using morphine.

Table XII contains the blood pressure and weight variation data that were taken. As can be seen there was no significant change in the blood pressure. The patient lost only eight pounds during the treatment. That is not significant in view of the length of time that he was in a delirious state. The weight was regained fairly rapidly.

TABLE XII

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
1-19-32	115/80	141.5	1-30-32	—	133.5
1-20-32	115/70	141.0	2-18-32	—	147.0
1-21-32	105/80	140.0	3-20-32	—	160.0
1-22-32	105/70	140.0	4-26-32	—	167.0
1-27-32	125/78	—			

Data on the kidney function are given in Table XIII. Here as in Case 1 the function became very low after two days. That this is not an artefact of technique seems more certain, in view of finding it again.

TABLE XIII

Date	cc. Urine First Hour	cc. Urine Second Hour	% of Dye eliminated First Hour	% of Dye eliminated Second Hour	Total % of Dye eliminated
1-19-32	180	50	88	9	97
1-21-32	140	15	30	2.9	32.9
1-22-32	90	85	65	15	80

Urinalysis data are presented in Table XIV. Here again one finds a preliminary drop in the specific gravity, followed by a rise. Toward the end of the fall the urine became alkaline. There was then a rise in the specific gravity which was probably due to the same causes as were mentioned in the study of Case 1. When the sodium rhodanate was stopped the specific gravity fell again.

TABLE XIV

Date	Appearance	Reaction	Sp. Gravity	Albumin
1-19-32	straw-amber	acid	1.026	Negative
1-21-32	cloudy straw	acid	1.016	Negative
1-22-32	cloudy amber	alkaline	1.015	Negative
1-23-32	cloudy straw	alkaline	1.029	Negative
1-26-32	cloudy straw	acid	1.035	Negative
2-1-32	cloudy amber	acid	—	Negative
2-2-32	cloudy amber	acid	1.020	Faint trace
2-3-32	cloudy amber	alkaline	1.019	Faint trace
2-4-32	cloudy straw	alkaline	1.009	Negative
2-5-32	cloudy amber	acid	1.011	Negative
2-6-32	clear straw	acid	1.012	Faint trace
2-7-32	clear amber	acid	—	Negative
2-8-32	clear straw	acid	1.025	Faint trace
2-9-32	clear straw	acid	1.023	Negative
2-10-32	clear straw	acid	1.020	Negative
2-11-32	clear straw	acid	1.024	Negative
2-12-32	cloudy amber	acid	1.028	+
2-12-32	clear amber	acid	—	Faint trace
2-15-32	cloudy amber	acid	1.030	Faint trace
2-16-32	clear straw	acid	1.020	Trace

The data seem to show that when agglomerating agents were in the body with the peptizing agents the specific gravity fell. This may be because the peptizing agents were being utilized to a greater extent at that time.

In Table XV are found the hematological data. As in Case 1, the total white cell count was normal with a relative lymphocytosis at the start of the treatment; then a polymorphonuclear leucocytosis developed, and shifted to a lymphocytosis as the number of white blood cells decreased.

TABLE XV

Date	W.B.C.	Polys.	Lymps.	Monos.	Eosins.	Basos.
1-20-32	6,650	64%	35%	1%	—	—
1-21-32	7,900	60%	36%	4%	—	—
1-22-32	7,000	56%	43%	1%	—	—
1-25-32	15,000	80%	17%	3%	—	—
1-26-32	14,000	63%	34%	3%	—	—
1-29-32	10,800	59%	39%	2%	—	—

Psychological tests were given to the patient at various times. The data on the test of crossing out the letter "O" are given in Table XVI. As morphine was withdrawn the patient was slower at crossing out the letter "O" and more accurate. After rehabilitation he was much faster, and at the same time less accurate. On January 19th the test was given before a dose of morphine was due; and on the 20th just after a dose of morphine was given.

TABLE XVI

Date	Number of O's	Number missed	% Accuracy	Time in Seconds
1-19-32	50	2	96	130.8
1-20-32	50	0	100	140.0
1-22-32	50	1	98	143.4
3-20-32	50	3	94	98.8

The dictation test was given to the patient also. From Table XVII it can be seen that there was no severe disturbance, resulting from the withdrawal of three-quarters of the morphine under the influence of sodium rhodanate. Upon rehabilitation, the patient performed the test better in all respects.

TABLE XVII

Date	Space taken in lines	Number of words	Number of mistakes	Time in seconds	Remarks
1-19-32	30.5	84	1	176.2	Writing hardly legible
1-20-32	29.5	84	1	159.8	Writing more legible
1-22-32	31.25	84	4	180.0	Writing hardly legible
3-20-32	27.5	84	0	155.2	Writing legible

A word-association test was given to the patient. The test contained fifty words; an attempt was made to include about ten key words. It was often found that the patients reacted to words that were not meant to be key words. The reactions and time of response to each word were taken. The data are presented in Table XVIII. The words that were not associated well and those that took a longer time to associate are given in the table. It is interesting to note that as the treatment progressed, the patient performed the test more rapidly. The word morphine did not stir the patient up much after the treatment began. After rehabilitation it did not bother

TABLE XVIII

Date	Word	Response	Time in Seconds	Sum in Seconds of Times for 50 Words	Remarks
1-19-32	Woman	Table	3 0	103 3	No response to such words as: Knife Murder Suicide Syringe Home Prison Hospital
"	Morphine	Amytal	13 8		
"	Children	Woman	2 8		
"	Addict	Morphine	2 2		
"	Hotel	Langwell	5 0		
"	Doctor	Fakir	2 4		
"	Road	Rose	1 8		
"	Cuff	Leather	1 8		
1-20-32	Drawer	Box	2 0	83 .	The word morphine elicited no special response, nor did the words Hotel and Woman
"	Addict	Morphine	2 0		
"	Water	Faucet	2 2		
"	Prison	Auburn	2 8		
"	Robe	Fur	2 0		
"	Intercourse	Yes	2 2		
"	Shield	Steel	2 0		
"	Tray	Platter	2 0		
"	Salesman	Bonds	2 2		
"	Hospital	Nurse	2 0		
"	Cocaine	Dope	1 8		
"	Brace	Foot	2 3		
1-22-32	Line	String	2 2	84 6	Word after Woman Very rapid These three words followed in order
"	Morphine	Dope	2 4		
"	Bed	Pillow	4 8		
"	Intercourse	Up	2 6		
"	Doctor	Medicine	1 4		
"	Insane	Crazy	1 0		
"	Cocaine	Dope	1 2		
"	Brace	Get up	3 2		
"	Wire	Steel	1 0		
2-20-32	Morphine	Dope	1 2	77 8	Very rapid These three words followed in order Again there is a mix-up caused by cocaine
"	Woman	Man	1 2		
"	Faucet	Water	1 0		
"	Drawer	Box	2 0		
"	Prison	Convict	2 0		
"	Hotel	Meals	2 4		
"	Doctor	Physician	1 4		
"	Hospital	Sick	2 0		
"	Cocaine	Dope	1 5		
"	Brace	Iron	2 8		

him at all. On the other hand, the word cocaine gave rise to a delayed reaction every time that it was given. That brings up the question of his delirium, which was the longest one that any patient has had. Cocaine addicts often go into a delirium when they are withdrawn. When he was admitted, this patient was injecting a solution about which there was some mystery. He said at the time that it might have contained cocaine. The association test indicates that cocaine was on his mind. So, the delirium upon withdrawal (but not the psychosis which followed) may have been due to cocaine.

In summary, the only ordinary withdrawal symptoms that the patient exhibited were: vomiting, restlessness (hyper-motor activity and nervousness), loss of weight and appetite, twitches, and aching in the back and legs. The aching and vomiting were the only things that bothered him. After he had cleared from the psychosis he said that he did not suffer during withdrawal. He did not smoke much after the morphine was withdrawn. Everything considered, the prognosis seems good.

Case 3, C. B.

This patient was a physician, 48 years of age, who had been using morphine for about six years. When admitted to the hospital on January 24, he said that he was using four grains of morphine every twenty-four hours. He became addicted to morphine in an attempt to break an alcohol habit. He claimed to have withdrawn himself once, but was not able to refrain from using morphine for any length of time.

Upon admission to the hospital, the patient's belongings were taken from him, and a special nurse assigned to the case. It became evident in a short while that he was not a normal person in other ways than would be accounted for by morphinism. He was five feet eight inches high, and weighed 190 pounds. His countenance, while inclined to be jolly at times, more often was expressionless. The patient said that he was well-to-do. Later information showed that his financial status was not good, although it had been. Though he made no attempt to cover his identity, he said that he lived in one city, whereas actually he lived in another a hundred miles away. It was difficult to elicit information from him; and when it was forthcoming one often wondered whether or not it was accurate. Although he was a physician, and said that he was immediately upon arrival, he did not appear to be conversant with common medical terms and remedies. All efforts to make him talk on such subjects failed consistently; because he claimed generally that the things spoken of were not familiar to him.

A physical examination revealed several interesting things. His nutrition was adipose. There was considerable adipose tissue around the lower part of the face, neck, and limbs. The pupils of his eyes exhibited a sluggish response to light and accommodation. There was an ulcerated, necrotic sore on the right thigh measuring about two by three inches, and more than one-quarter of an inch deep. The origin of this could not be determined. At first the patient claimed that it came as a result of an automobile accident.

A month or so later, he said that it was the result of an injection of potassium cyanide. This gives something of a picture of the mental condition of the patient. The teeth were regular but a spacing between them was noticed. There was an extensive chronic gingivitis and expressed pus in various places. The nasal mucous membranes were somewhat congested. His tongue was heavily coated and extended in the mid-line with a very slight tremor. His fauces and pharynx were slightly congested.

The patient was of the eunuchoid type, as shown by the hair distribution on his body, very small genitals, and the formation of breasts. When excited his voice reached a high pitch. The pubic hairs ended abruptly. The hair on his head was thin; but he had a normal beard. There were folds of fat on his wrists; and he was heavy jowled. About ten years previously he suddenly gained a good deal of weight which he did not lose.

The plan for this experiment was altered from that of the previous two. It was decided to reduce his dosage of morphine to about half of what it was upon admission to the hospital, and attempt to keep him comfortable for a few days with small amounts of sodium rhodanate. Table XIX shows how the morphine dosage was reduced, and the amounts of sodium rhodanate used.

TABLE XIX

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-25-32	1 50	0 00	1-20-32	0 25	2 33
1-26-32	2 25	0 67	1-30-32	0	3 33
1-27-32	2 00	2 33	1-31-32	0	2 00
1-28-32	1 50	2 67	2- 1-32	0	1 00

January 25, 1932.

In the morning the patient had a good appetite, and no complaints. He passed a fairly comfortable day. From 10:30 p.m. until midnight he was very restless. A headache bothered him during this time, also.

January 26, 1932.

The patient did not sleep until after 2:00 a.m., when one-half grain of morphine was given. He then slept for about four hours. From the restlessness on January 25, it was decided that a reduction in the morphine from four grains a day to one and one-half grains was too much. That is why the dosage was increased on this day. As a result of the increased dosage, the patient passed a more comfortable day. Ten grains of sodium rhodanate were given at 10:00 p.m. in an effort to help the patient sleep. Two Alophen tablets were given at 8:00 p.m.

January 27, 1932.

Five grains more of the sodium rhodanate were administered at 12:30 a.m. Despite the peptizing agent, the patient was very restless and unable to sleep. To one inexperienced in sodium rhodanate therapy the two nights of restlessness and little sleep would indicate that the method of treatment

was falling down. There might be a strong tendency, in some quarters, to let the matter go at that. The successful use of sodium rhodanate requires both a thorough knowledge of the theory upon which it is based, in addition to a touch of "scientific backbone." With that in mind the case was carried on, giving sodium rhodanate to effect. While the restlessness was not very great, still it was not desirable to encounter it so early in the withdrawal. This indicates some of the difficulty that one might have upon attempting abrupt withdrawal with the help of sodium rhodanate. The peptizing agent is not so efficient in its function as morphine is as an agglomerating agent. It seems probable from these considerations that a high concentration of sodium rhodanate must be built up in the system before it becomes a useful aid in combatting withdrawal symptoms. Reference to the adsorption isotherm, pictured in any good book on colloid chemistry, will make this point clear. Therefore it would be inadvisable to attempt to commence medication and abrupt withdrawal coincidentally.

The patient was given one-half of a grain of morphine at 6:30 a.m.; that was followed by five grains of sodium rhodanate. He refused breakfast although he had no complaints other than being tired and sleepy. One-half of a grain of morphine was administered at 11:05 a.m.; following that five grains of sodium rhodanate were given. At 4:00 p.m. one-quarter of a grain of morphine was given, followed by five grains of sodium rhodanate.

He passed a quiet, comfortable day, except for the early morning, and an hour between 6:30 and 7:30 p.m., during which he was restless and nervous. He was fairly quiet at the latter hour. At 8:00 p.m. he complained of pain around the heart. He became nauseated, and vomited undigested food at nine o'clock. Following that, he was more comfortable. Ten grains of cascara were administered at 9:20 p.m. By ten o'clock the patient was very quiet and asked that his morphine hypodermic be delayed. Fifteen grains of sodium rhodanate were administered at this time. One-half of a grain of morphine was given at 10:45 p.m. At 11:30 p.m. he was quiet, but was not able to sleep.

It was found that the patient was exceptionally suggestible. The mental peculiarities that were noticed in the pre-treatment study were not changed at this time. He said that he did not feel the morphine "take hold" as it used to; but it quieted him, nevertheless.

January 28, 1932.

From 2:30 to 5:30 a.m. the patient slept lightly at intervals. He was somewhat restless after that. He slept very little; at the same time he was not nervous or restless until 5:30 a.m. At 6:30 o'clock one-half of a grain of morphine was given, followed by ten grains of sodium rhodanate. At nine o'clock in the morning he appeared to be very comfortable. He was given one-quarter of a grain of morphine, and five grains of sodium rhodanate at 1:00 p.m. Ten grains more of the peptizing agent were given at 4:00 p.m. The patient was comfortable and had no complaints throughout the day and evening except those that are indicated. At supper time his appetite

was poor. He vomited at 5:30 p.m. One-quarter of a grain of morphine was administered at six o'clock. Near midnight the patient's face became slightly flushed. He did not feel sleepy at this time.

At 9:30 p.m. he was given two Alophen tablets. One-half of a grain of morphine was administered at ten o'clock; this was followed immediately by fifteen grains of sodium rhodanate.

January 29, 1932.

At times during the night, the patient was very restless. He was quiet the greater part of the night. Like many people using really large doses of sodium rhodanate, he complained of having bad dreams. From 5:45 to 7:00 a.m. he perspired moderately when awake. The patient took the regular hospital diet in the morning and at noon.

Despite a substratum of apprehension the patient was comfortable until 4:30 p.m. when he complained of nausea. He did not eat heartily at 5:00 p.m. The patient had no special complaints at 6:00 p.m.; after having spent most of the day in bed. He vomited once, shortly after six o'clock. During the early part of the evening he was very nervous. After 10:15 p.m. he quieted down, and was fairly comfortable. At no time did he thrash around in bed. He did not become nervous to the extent of exhibiting hyper-motor activity. After 11:30 p.m. he slept at long intervals.

The medication for the day was as follows: ten grains of sodium rhodanate at 11:00 a.m. and 4:00 p.m., and fifteen grains at 10:00 p.m., one-quarter of a grain of morphine at 6:30 p.m.

January 30, 1932.

At 3:30 a.m. the patient awoke suddenly, and was confused. He complained that it was difficult to walk. He exhibited difficulty in holding a glass while drinking. He moaned in his sleep. Ten grains of sodium rhodanate were given at 3:30 a.m. He complained of abdominal cramps during the early morning. Upon awakening at six o'clock, he was confused and irritable, but not nervous. Ten grains of sodium rhodanate were given at 7:00 a.m.

The patient ate fairly heartily at 7:30 a.m., and then slept at intervals for about an hour. At nine o'clock hallucinations of sight were evidenced. He talked, in a quiet way, a good deal about women and millionaires. Definite delusions of grandeur were exhibited. The patient seemed confused until 10:00 a.m. He was given ten grains of sodium rhodanate at eleven o'clock. He refused the regular diet at noon.

The patient was not nervous or restless all day long. He stayed in bed, and had very little to say. There were no signs whatever of distress. Five grains of sodium rhodanate were given at 4:00 p.m., and fifteen grains at 10:00 p.m. The afternoon and evening were uneventful; the patient was rational and quite cheerful at 11:00 p.m.

January 31, 1932.

He slept from 12:30 until 3:00 a.m.; he moaned and talked a great deal during his sleep. At three o'clock he awoke dazed, irrational and irritable.

He was unable to stand when out of bed. An involuntary bowel movement occurred at this time; another occurred an hour later. Considerable mucous accompanied both movements. The patient slept quietly from 4:30 to 7:00 a.m., at which time there was another involuntary bowel movement. Five grains of sodium rhodanate were given, at this time. He refused nourishment until noon. The patient slept quietly off and on throughout the morning.

The delusions and hallucinations of sight persisted. When asked if he knew that he was having involuntary bowel movements, he replied that he did. He stated that he knew beforehand when they were coming; but he did not care enough to call the nurse. The patient was lethargic and had been more or less so for some time prior to this treatment. He talked very little during the day; he refused to swallow medication (sodium rhodanate, five grains) at 4:00 p.m.

The patient was quiet throughout the day. There were some muscular twitches about which he did not complain; but he was not nervous or restless. There was another "involuntary" bowel movement during the evening. The word involuntary is put in quotation marks because the act appeared to be due more to laziness and apathy than to loss of sphincter control. Fifteen grains of sodium rhodanate were given at 10:00 p.m. By 11:30 p.m. he was asleep.

February 1, 1932.

From 12:30 to 3:00 a.m. he talked constantly, and was very much confused. He did not sleep much during the night; but he was neither nervous nor restless. During the early morning the confusion seemed to come in waves. The patient was given five grains of sodium rhodanate at 7:00 a.m. He refused it during the rest of the day, along with other medication and food. The patient was quiet throughout the day. There were no complaints. He was not normal mentally. He only had one "involuntary" bowel movement. He did not want anyone to talk to him or disturb him in any way.

February 2, 1932.

Another "involuntary" bowel movement occurred at 2:40 a.m. He slept quietly at long intervals during the morning hours. Except that he seemed slightly more rational in the morning, his condition was unchanged. From the beginning of the psychotic condition, for several weeks the patient refused to feed himself. His appetite was better on this day.

At about 9:30 a.m., the patient had a ten-minute sinking spell. His pulse became slow and weak, and his lips cyanosed. The pupils of his eyes were dilated. This occurrence did not take place again.

It was noticed that the patient seemed frightened at times, about 4:00 p.m. Shortly thereafter he said that he was going to jump from an airplane. This was in the midst of confusion which continued unabated during the day. The patient was unquestionably suicidal, as he had been before treatment (the avowed injection of potassium cyanide). There was an "involun-

tary" bowel movement at 9:00 p.m. He said that he was going to die, for several days.

After a consultation with a psychiatrist concerning the condition of the patient, it was decided that there were three possibilities. Over-peptization with sodium rhodanate might have accounted for the mental symptoms. On the other hand, the patient might have had a brain tumor. The third possibility was that the psychotic condition might have been due to the misfunction of the endocrine glands. The first possibility had in its favor the fact that the patient had been given large amounts of the peptizing agent; and other patients had gone that way. Against that hypothesis was the fact that in the two days preceding this one, sodium rhodanate did not make the condition worse. Also, the psychotic condition was not typical of those that have been observed as the result of over-dispersion. Delusions of persecution were not a large part of this picture, while delusions of grandeur were. No motor excitement accompanied the condition. The possibility of a brain tumor was ruled out largely from the fact that an X-ray study revealed nothing; in this study an examination of the skull in both right and left lateral position revealed a normal sella turcica. A Wassermann test was negative. Table XX shows the result of a blood examination. The data reveal no abnormalities.

TABLE XX

Factor	Mg. per 100 cc. Blood	Normal Values Mg./100 cc. of Blood
Sugar	110	90-120
Urea Nitrogen	7.7	7-15
Calcium	9.8	9-11.5

The third of the above possibilities was suggested by the fact that the man was of the eunuchoid type. Several things were noticed in the physical examination (which see) that suggested hypopituitarism. In Table XXI are given the results of basal metabolic rate determinations. The data indicate a tendency to hypothyroidism. That left the possibilities of endocrine misfunction and over-dispersion to be investigated. The condition of the patient was considered to be due either to one or the other of these two things. It was easiest to test the over-dispersion hypothesis first. To that end, three grains of sodium amytal were given by the mouth at 10:35 p.m. He did not talk except to answer questions.

TABLE XXI

Date	Basal Metabolic Rate	Remarks
1-25-32	-19	Normal is ± 10
1-28-32	+23	Patient nervous due to withdrawal
3-21-32	-8	After attempting to raise rate.

February 3, 1932.

The patient had two "involuntary" bowel movements during the early morning hours, and another at 7:20 a.m. He slept well, however. No medication was given during this day. In the afternoon, the patient was rational at times. He would not talk except to answer questions and say irrational things. It was at about this time that he began to speak about the rays that were coming from the wall of the room. The rays carried messages to him. In addition, he stated that his abdomen was filled with helium.

There was no definite improvement in the condition of the patient.

A day by day report from this point on will not reveal enough to justify it. Therefore, a general description of the treatment and the patient's reaction will be given.

On February 4 and part of the 5th ipral and sodium amytal were given in order to make a final decision as to whether or not the patient would improve on agglomerating drugs. It should be mentioned that while the patient was able to be out of bed, he resisted efforts to induce him to do so. This was probably due to a general lethargy. Until the day that he was discharged he would always have preferred to remain inactive in bed. Later he did become more tractable and stay out of bed for longer intervals; but it always required an effort to keep him out of bed. Toward the end of his stay in the hospital, this appeared to be due more to plain laziness than anything else. No definite improvement was noticed as a result of the use of agglomerating agents.

Before making a final shift to a diagnosis of endocrinopathy, it was decided to be doubly certain that sodium rhodanate in fairly large quantities would not change the situation. Between 6:00 p.m. on February 5, and the same hour on February 8, one hundred forty grains of sodium rhodanate were administered. This had no effect other than to make the patient somewhat more irritable, and give him more sleep at night. The "involuntary" bowel movements, lethargy, and irrational condition, along with the delusions persisted, and became neither better nor worse. If the psychotic condition had been brought about by over-dispersion, or the use of sodium rhodanate, it seems fair to assume that sodium rhodanate would have made it worse. Since it did not change when fairly large quantities of the dispersing agent were given, the conclusion was drawn that it was not brought about by over-peptization. From what has been said of the case it seems apparent that the psychosis pre-dated the treatment. In all probability the starting point of the mental upset came prior to the chronic use of alcohol which latter led the patient to take morphine. In other words the drug largely covered up the mental imbalance.

It will be remembered that Lang and Paterson¹ found that it was not easy to produce changes by agglomeration and dispersion in the one endocrinopathy case that they studied. It was decided finally that this patient

¹ J. Phys. Chem., **35**, 3425 (1931).

was upset by hypothyroidism and hypopituitarism; and that it was not at the moment primarily a case to be treated by peptizing and agglomerating agents.

From the date of admission until February 4, the patient ran a fever which averaged 99° F. From the 4th to the 9th of February, his temperature averaged 98.4° F. The average was 100.2° F. from the 9th to the 16th. It went down slowly from the 16th to the 26th. The average from the 26th to the 7th of March was 99° F. From the 7th of March to the 25th the average was 98.4° F.

Treatment for the hypo-endocrine function was started on the 11th of February. Pituitary body (anterior lobe) emplets were used; four grains were administered daily until the patient was discharged. Thyroid gland emplets were administered; two grains per day were given. The patient was a little brighter by February 13; the "involuntary" bowel movements continued. The psychotic condition remained unimproved. The patient made somewhat more of an effort to help himself, however. Iron, quinine, and strychnine was given as a tonic. On the 14th of February, the patient began to perspire freely; a day later the reaction became profuse and then subsided.

By the 17th of February definite improvement was seen in the condition of the patient. No one of his symptoms had subsided a great deal, however. Some periods of restlessness were observed. The administration of thyroid gland emplets was reduced by half on February 19, and discontinued on February 20. This measure was taken because his pulse rate began to go above 100 consistently. After the 18th of February there were no more "involuntary" bowel movements. At the same time the patient became more cooperative. On the 23d and 24th of the month the patient complained of nervousness, and his mental condition was back-sliding slightly. From this time until he was discharged, one month later, three five-grain doses of sodium iodide were given daily. There were two reasons for this. In the first place stimulation of the thyroid gland was indicated; and secondly, by its peptizing action it was of use in allaying nervousness.

On February 26, the patient was somewhat brighter. He was taken for an automobile ride. The next day additional endocrine treatment was instituted. Nine "Testacoids" tablets¹ were given daily in three equally divided doses until the patient was discharged from the hospital. On the 29th he stated that he knew he was mentally upset. By March 2d the patient was decidedly more active and clearer mentally. The change was easily noticeable; and, as is evident, it came shortly after the start of the "Testacoids" medication. Daily improvement was the rule from that time on. He began to talk voluntarily; expression came into his face; he was less lethargic (although it was still difficult to keep him out of bed); and the psychosis was practically a thing of the past by the 7th of March. When asked what he was being treated for he said probably pituitary gland inefficiency. This

¹ Reed and Carnrick Co. orchitic extract.

indicates that he knew that he had such a condition before withdrawal. When asked what he remembered after withdrawal, it was discovered that the experience was a blank in his mind. He claimed to have suffered no pain or distress during the treatment; and he was not observed to have any.

Were it not for the fact that there are people who are a bit too willing to condemn peptization therapy, no special effort would be made to establish the fact that this endocrine condition pre-existed the treatment for morphinism by quite a while.

By the 10th of March, the patient was taking a much greater interest in things. From March 8 to March 13, the patient was given Antuitrin hypodermically in place of the pituitary body emplets in order to obtain a greater efficiency from the drug. The patient began to complain bitterly that he did not care to have injections made because of his experience with morphine.

TABLE XXII

Date	Blood Pressure	Weight in Pounds	Date	Blood Pressure	Weight in Pounds
1-25-32	—	190	2-16-32	120/70	—
1-26-32	140/80	190	2-18-32	118/75	—
1-27-32	135/75	—	2-25-32	120/70	—
1-28-32	—	190	3-21-32	—	175
2-10-32	120/70	—	3-25-32	128/80	—

A shift was made to the emplets again. Despite the fifteen grains daily of sodium iodide the patient was not sleeping well at this time. From the 15th to the 20th of March the sodium iodide was augmented by ten grains of sodium rhodanate at bed-time. This allowed him to have longer and more sound sleep. Thereafter sodium rhodanate was given in ten-grain doses as needed.

The patient was discharged on March 25. At that time he was brighter and less lethargic than he was upon admission. His mind was definitely clearer than it was before morphine was withdrawn. There was a natural laziness that still had to be combatted. So far as could be determined there was no mental or physical need for morphine. He was instructed to continue the use of the pituitary extract and "Testacoids" for an indefinite period. Sodium iodide was to be taken for a few weeks, and then discontinued. Sodium rhodanate was to be used only as needed to combat sleeplessness and nervousness.

Table XXII shows the blood pressure and weight data that were taken. While these data are rather sketchy, they do illustrate several things. January 29 was the last day that the patient had morphine. On the 28th he had lost no weight. He exhibited practically no withdrawal symptoms, and his appetite did not fail until the psychotic symptoms appeared. The patient did not lose weight during the withdrawal period. Therefore, watching the patient, it was obvious that he lost most of his weight during the period when thyroid extract was being given. In fact it was planned to have him lose weight at that time. The drop in blood pressure during the treatment

was probably due to the nervous relaxation afforded by the sodium rhodanate. That the blood pressure remained low indicates that there were no arterio-sclerotic changes. It should be pointed out that the initial systolic pressure was the highest that has been observed in the eight cases of morphinism that have been studied.

TABLE XXIII

Date	Appearance	Reaction	Specific Gravity	Albumin
1-25-32	cloudy amber	alkaline	1.027	Very faint trace
1-26-32	cloudy straw	alkaline	1.016	Negative
1-27-32	cloudy straw	alkaline	1.017	Negative
2-1-32	clear amber	acid	—	Negative
2-3-32	clear amber	acid	—	+
2-4-32	clear amber	acid	1.029	+
2-5-32	clear amber	acid	1.030	+
2-6-32	clear amber	acid	1.030	+
2-9-32	clear amber	acid	1.030	+
2-10-32	clear amber	acid	1.026	++
2-11-32	cloudy straw	acid	1.030	Faint trace
2-13-32	cloudy amber	acid	—	Trace
2-17-32	cloudy amber	acid	1.020	+
2-20-32	cloudy straw	alkaline	1.016	Negative
3-18-32	cloudy straw	acid	—	Negative
3-19-32	amber	alkaline	1.019	Negative
3-21-32	cloudy straw	acid	—	Negative
3-23-32	straw	alkaline	1.020	Negative

TABLE XXIV

Date	cc. Urine First Hour	cc. Urine Second Hour	% Dye eliminated First Hour	% Dye eliminated Second Hour	Total % Dye eliminated
1-27-32	360	150	52	18	70
1-28-32	350	130	47	14	61

In Table XXIII the urinalysis data are presented. In these data there appears again a preliminary drop in the specific gravity followed by a rise after continued administration of sodium rhodanate. From the data, the alkalizing effect of sodium rhodanate does not appear, as it did in Cases 1 and 2. The albuminuria indicated during the two weeks beginning March 3 was not so pronounced as the data appear to make it, for the readings of the Tompkins County Laboratory are on a high scale. Sugar was not found at any time.

Although only two kidney function tests were made, the data, in Table XXIV, suggest an early drop in the function like that found in the previous two cases. There was no reason to suspect that the renal function did not rise again.

The three hematological studies that were made showed only three things. The blood count was normal at the start of the treatment; there was not the usual relative lymphocytosis. On the last day that morphine was given a polymorphonuclear leucocytosis had developed with a total white cell count of 13,600.

The psychological tests on this patient gave very interesting results. The data for the test of crossing out the letters "O" are given in Table XXV. The results of this test show that during the first three days of the withdrawal, the patient was faster and more accurate. Shortly before he was discharged from the hospital, the patient was a great deal more accurate and somewhat faster. He had not reached normal accuracy however. He was more co-operative in securing the data also. It would seem, from the above data, that sodium rhodanate brought about better nervous function during withdrawal; and endocrine and sodium rhodanate therapy caused a great deal of improvement.

TABLE XXV

Date	Number of O's	Time taken in seconds	Number Missed	% Accuracy
1-25-32	52	74.0	29	44.4
1-27-32	53	68.8	17	67.9
3-21-32	53	63.2	10	81.1

The word-association test was performed with very interesting results. Table XXVI contains the data. After the first day the patient was much more rapid in his associations; also, there were not so many queer replies. The rate of association did not increase appreciably during convalescence. These tests seem to indicate that the mind of the patient became clearer after sodium rhodanate therapy was instituted.

In summary, this patient was withdrawn in five days from a daily dose of four grains of morphine, without any more than a transient appearance of withdrawal symptoms. There were no distressing withdrawal symptoms; had it not been that the patient was somewhat nervous at times upon a daily dosage of two and one-half grains of morphine, one would have suspected that he was not a drug addict at all, so far as withdrawal symptoms went. When morphine was cleared out of him a pre-existing psychosis developed which was traced to faulty endocrine function. The condition was treated by endocrine therapy. The patient improved and was discharged with neither a need nor a desire for morphine. The prognosis for continued abstinence from morphine seems to be good.

Case 4, C. W.

The patient was a male physician, 49 years of age, who had been addicted for about eighteen years. When admitted to the hospital he was using about six grains of morphine daily. Sciatica was the ostensible cause of the original addiction, along with nervousness and insomnia. The number of treatments that he had taken could not be ascertained. A few years ago, he attempted to blow his brains out with a revolver, but missed the mark entirely.

TABLE XXVI

Date	Word	Response	Time in Seconds	Total time for test in in Seconds	Remarks
1-25-32	blotter	ink	4 4	181 6	
"	glass	plate	5 6		
"	morphine	getting over it	31.6		
"	addict	many	3 0		9 response words
"	porch	winter	4.0		ending in "ing"
"	leg	mutton	4 6	}	These 3 words followed in order
"	suck	calf	4.6		
"	eraser	blotter	9 8		
"	clip	hair	4.0	}	These words oc- curred together
"	murder	terrible	5.8		
"	trolley	passenger	5 0		
"	asylum	awful place	5.8		
"	spoon	celluloid	2.4		
"	anesthetic	ether	1 8	}	These words followed in order
"	fire	wood	7.0		
"	suicide	shooting	8 2		
1-27-32	morphine	addicts	1 8	79 9	
"	addict	morphine addicts	1.8		Not so many
"	eraser	rule out	2 0		peculiarities in
"	nurse	trained	2.4		this test
"	chart	memory	1 4		13 response words
"	murder	many	2.0		ending in "ing"
"	asylum	insane	1 4	}	These words oc- curred together
"	wall	room	3 6		
"	suicide	murder	2.4		
3-21-32	morphine	addict	1 4	78.9	13 words ending
"	leg	right leg	1.4		in "ing"
"	suck	calf	3 0		
"	addict	morphine	1.2		
"	nurse	trained	1.6		
"	intercourse	relations	4.2	}	These words followed one another
"	ink	writing	1 0		
"	auto	car	2 8		
"	murder	killing	2.0		
"	asylum	insane	1.4	}	These words occurred together
"	wall	stone	2.8		
"	desk	writing desk	1.6		
"	suicide	murder	1.6		

Upon admission to the hospital the patient was very nervous; his speech particularly betrayed his nervousness. He was so nervous that he stammered. Psychomotor hyperactivity was a part of the general picture. He looked tired and had a cold. As with the other cases, the patient's clothes and all belongings which could serve to conceal morphine were taken from him, and locked up. The patient was then put to bed in a private room. As with the other patients no visitors were allowed except when a nurse was present.

Physical examination revealed very little that was abnormal. The patient was five feet ten inches tall, and weighed 160 pounds; there was a good moderate amount of subcutaneous fat over the entire body. His blood pressure was 115/80. His teeth were in poor condition, apparently as a result of neglect. The pharynx was congested mildly. The patellar reflexes were hyperactive and equal.

TABLE XXVII

Date	Grains Morphine	Grams NaCNS	Date	Grains Morphine	Grams NaCNS
1-29-32	5.00	0	2-3-32	2.00	1.33
1-30-32	3.75	0	2-4-32	1.23	2.00
1-31-32	5.25	0.67	2-5-32	0	3.67
2-1-32	3.50	1.33	2-6-32	0	2.67
2-2-32	3.00	2.33	2-7-32	0	0.67
			2-8-32	1.00	0

The patient was admitted to the hospital at noon on January 28. No attempt was made to study him on that day. Table XXVII shows the dosages of morphine and sodium rhodanate that were administered while the patient was in the hospital.

January 29, 1932.

From midnight on, the patient slept for six and one-half hours. He passed a comfortable night. He was not so nervous as he was during the previous half day. The day was spent attempting to arrest the cold with which the patient was afflicted. Ammonium chloride and magnesium citrate were used to that end. He was slightly nervous during most of the day. Morphine was given in five doses.

January 30, 1932.

The patient slept for about six hours during the early morning. He was very nervous and restless when he awoke in the morning at 7:00 a.m. Despite orders to stay in bed because of his cold, the patient became restless and walked about in a nervous manner at 9:00 a.m. The patient passed a restless and only fairly comfortable day. It was obvious that he had been used to more than 3.75 grains of morphine per day. Treatment for the cold was continued, though no cathartic was given. His appetite was only fair.

January 31, 1932.

The dosage of morphine was raised in an effort to keep the patient more comfortable. He slept for five hours after 1:30 a.m. His appetite was better

in the morning. The patient was not so restless as he was during the previous day. The cold improved. Otherwise nothing unusual transpired.

Two Alophen tablets were given at night. Ten grains of sodium rhodanate were administered, by mouth as usual, at 11:00 p.m. The patient was given ammonium chloride at frequent intervals during the day.

February 1, 1932.

The patient awoke in a very nervous condition at 3:00 a.m., and complained of having had a horrible nightmare. He went to sleep again shortly. He passed a fairly comfortable night, and slept for about five hours. His appetite was better than it had been. At 3:15 p.m. the patient was very nervous. Again at 7:30 he had a nervous spell. If anything, the patient was less nervous and restless than on the previous day. No symptoms of withdrawal were seen. Sodium rhodanate was given at 8:00 a.m., and 7:00 and 10:00 p.m.

With this patient and others that followed, it was learned that it is most inadvisable to allow them to communicate with one another during withdrawal, for several reasons. They talk constantly of morphine, and their experiences with it. They all immediately exhibit any symptom that any one of them has. There is also a tendency to want to regulate their medication; though they know nothing about what doses are being administered.

February 2, 1932.

He slept well and passed a comfortable night. The patient was fairly comfortable throughout the day; although there were periods of restlessness and nervousness. Aside from that there were no complaints. The patient volunteered the information that the sodium rhodanate alone gave him a "kick," and then quieted him. The first part of his statement probably was a figment of the imagination. The second part was observed. His appetite was good at supper-time. Sodium rhodanate was administered at 5:00, 8:00, and 11:00 a.m., and at 2:00, 4:00, 8:00, and 11:00 p.m. The times of administration of the peptizing agent were arranged so that it was given one hour after each hypodermic of morphine.

February 3, 1932.

From midnight on the patient slept soundly, and almost continuously. About 10:00 a.m. he complained of abdominal cramps. This symptom disappeared in about an hour. There were periods during the day when the patient was nervous and restless; but the symptoms were not severe in any sense of the word. In the afternoon, he complained that the sodium rhodanate upset his stomach. That is not an unusual thing, even for normal people. Instead of discontinuing the drug, or reducing the dosage, ten grains of sodium bicarbonate were given with each dose. Had the sodium bicarbonate not ameliorated the condition it would have had to be tolerated; because the large doses of sodium rhodanate were necessary. The day was hardly different from the one preceding it. Sodium rhodanate was given only when it was needed.

February 4, 1932.

After 2:00 a.m., the patient slept soundly, and almost continuously, for nearly eight hours. The morning passed in an uneventful manner. At noon, the patient ate heartily. During the afternoon the patient was restless and nervous at times; beyond that no withdrawal symptoms were observed. The day was a fairly comfortable one *in toto*. The patient realized that his dosage of morphine was being reduced.

In the evening he was restless and walked around a good deal. Two mistakes were made at this time. In the first place, the patient was told that he had had only 0.73 grain of morphine during the last twenty-four hour period. From conversation with other addicts he learned that in some quarters it is usual to administer a final one-half grain "pick-up" dose of morphine at the end of the treatment. Shortly thereafter he demanded such a final dose. This was absolutely contraindicated because it made just so much more morphine to work against the sodium rhodanate, and to be cleaned out of the system. Since the man was a free agent, and cases were at a premium, and despite better judgment, the dose was given. In addition, that made the final reduction dosage a large one. The patient went to bed and slept from 11:30 until after midnight.

February 5, 1932.

At 12:30 the patient became nervous, and up and about feeling restless. To combat that fifteen grains of sodium rhodanate were given. The patient then slept soundly for almost seven hours. At 8:00 a.m. he did not care to eat breakfast because of nausea; he drank coffee and immediately vomited it. He was not so restless and nervous but that he was reading quietly at 9:30 a.m. He was dozing at 11:30 a.m. The regular noon diet was refused.

The patient complained of feeling chilly at 1:30 p.m.; he was put to bed and external heat applied. A half hour later he was more comfortable, except that he was quite restless and nervous. To quiet him, a grain and one-half of codeine was given hypodernically at 3:00 p.m. He was quiet and sleeping for about one-half hour thereafter. The day was rather an uncomfortable one. Fleeting signs of the symptoms of withdrawal were observed. The only thing that was a definite part of the picture was the restlessness and nervousness; those symptoms were more pronounced than on the previous day. He did not thrash around in bed, and was able to lie quietly therein. Morphine addicts are notoriously jealous of their own comfort, and this patient was no exception. Yet, very little attention was paid to him.

In the evening the patient was nervous and restless until ten o'clock; he slept for an hour after that. It does not seem extravagant to claim that no patient who is suffering greatly from withdrawal symptoms would sleep as much through the withdrawal period as this patient did. Upon awakening he had the fixed idea that the only way to be comfortable was for him to have chloral hydrate. Since this drug is an agglomerating agent, it was absolutely contraindicated at this stage of the treatment. However, the patient was obdurate, and absolutely satisfied that chloral hydrate was the only thing that

would help him in any way, despite patient reasoning with him. He had ceased to "get a kick" out of the sodium rhodanate. The patient grew adamant and demanded chloral hydrate, the alternative being to leave the hospital. It is quite obvious now that the patient should have either followed the theoretical treatment or been discharged. He promised to take chloral hydrate on this date and then go along on a reduced dosage, finally stopping its use entirely. After being given twenty grains of the agglomerating agent he slept from 11:30 p.m. until 3:30 a.m.

Sterile hypodermics containing a little novocaine were given at intervals during the day.

February 6, 1932.

Giving sodium rhodanate and chloral hydrate at the same time was tantamount to giving nothing at all since one is a peptizing agent and the other an agglomerating agent. While the local concentration of either one is high, from the adsorption isotherm, the effect of that drug may predominate for a while, provided also that the two drugs are about as strongly adsorbed. That is about as far as it goes.

The patient read from 3:30 a.m. until four o'clock; he then slept until seven o'clock. He refused breakfast, although he said that he felt better. The statement that he felt better in combination with his appearance classified him immediately as one who would be very difficult to keep away from morphine. The facies appeared like that of a man who had been drinking whiskey all night long; it was gray and lined with nervous tension in contrast to the relaxed more healthy appearance that it had during withdrawal. He stammered consistently for the first time since the day that he was admitted to the hospital. There was psychomotor hyperactivity in addition, another symptom which had been under pretty good control during sodium rhodanate therapy. The man was what we choose to call a "pathological thrill-seeker."

As the morning wore on his appearance became better; the facies relaxed; the psychomotor hyperactivity subsided; and some color came into his face. Just as he finally threw off the effects of the chloral hydrate, he became very nervous and restless and demanded more of the drug, despite the fact that he said that he would only require it at night, and then in decreasing doses. The patient evidently had to feel euphoric. He became more nervous and restless and finally excited when the agglomerating agent was refused. Twelve grains had to be administered at 4:00 p.m.

During the day he complained of a feeling as though worms were crawling around in the epigastric region. This made him very nervous; but it quieted down completely when the upper abdomen was massaged in the region of the solar plexus. Despite all of this the patient passed a fairly comfortable day. He demanded twenty grains more of chloral hydrate at 9:15 p.m.; he was very nervous at the time. The patient slept from 9:30 p.m. to 12:30 a.m. He refused the regular diet throughout the day.

February 7, 1932.

He awoke at 12:30 a.m. and called for more chloral hydrate; he was very nervous. It was apparently taking more chloral hydrate to bring about euphoria which the patient desired, as the morphine was working out of his system. The patient slept well during the early morning. When visited during the morning, the patient was in the same condition as that described for February 6: ashen face, showing nervous tension, and psychomotor hyperactivity accompanied by stammering. When the condition wore off at around 2:30 p.m., he started his demands for chloral hydrate again. Six grains of the drug were given at 2:30 p.m. and again at midnight did not give him the "kick" that he sought. In addition he refused sodium rhodanate during the day.

TABLE XXVIII

Date	Appearance	Reaction	Specific Gravity	Albumin
1-29-32	cloudy amber	alkaline	1.019	negative
1-30-32	clear amber	acid	1.013	negative
2- 1-32	clear amber	acid	1.012	negative
2- 2-32	clear amber	acid	1.010	negative
2- 3-32	cloudy amber	acid	1.009	faint trace
2- 4-32	clear amber	acid	1.014	negative
2- 6-32	cloudy amber	acid	1.012	trace
2- 7-32	cloudy amber	acid	1.026	negative
2- 8-32	cloudy amber	acid	—	negative

February 8, 1932.

No medication was given on this day other than castor oil for the relief of constipation. In the early afternoon the patient requested that he be given one grain of morphine and discharged. Because he was a "pathological thrill-seeker" and apparently not very much interested in conquering morphinism his requests were granted. It is interesting to note that there was enough sodium rhodanate in the patient to cause the one grain of morphine to have greater than the normal amount of exciting action.

Table XXVIII gives the urinalysis data for this patient. Here again there is a preliminary decrease in the specific gravity, followed by a rise as the sodium rhodanate is eliminated along with increased amounts of sodium chloride. There was no sugar present at any time.

The one hematological study that was made upon admission showed a polymorphonuclear leucocytosis with a white blood cell count of 13,000. On the same date a test of the kidney function yielded a value of 69% of the dye eliminated in two hours.

That the laboratory studies on Cases 3 and 4 were not more complete was due to the failure of the Tompkins County Laboratory to cooperate in this work. Dr. Howe has commented on the situation recently.¹

¹ Ind. Eng. Chem., **24**, 479 (1932).

Discussion

In order to compare the withdrawal symptoms in these four cases with those seen when no drugs are used, it seems worthwhile to set down some of the findings of Lambert's Committee.¹

"In order to compare different treatments it is important to know the characteristic symptomatology and reactions of drug addicts to the withdrawal of their narcotic drugs. These are varied, but surprisingly distinctive, and more or less uniform in the majority of cases.

"For the best picture of unaltered withdrawal symptoms we have used our observations of one hundred control patients who received injections of innocuous solutions at regular intervals after their morphine dosage was abruptly withdrawn, until all withdrawal symptoms were over. In these cases we see the characteristic symptoms in their full intensity over a shorter period of time.

"In general it is possible to subdivide the symptoms of the drug addict undergoing withdrawal of his accustomed narcotic into two groups: (1) Physical symptoms, (2) psychic symptoms. A great many of the physical withdrawal symptoms seen in human addicts are presented in experimentally addicted animals (dogs usually), but in human addicts a very important psychic factor is superimposed, making the problem of withdrawing a human addict considerably different from that of an animal.

"Withdrawal symptoms may be subjective or objective.

"In addition, the physical symptoms may be *real*—or they may be affected by the psychic factor so that they may be *simulated*. Still further they may be *exaggerated* or *minimized* deliberately.

"If simulated or exaggerated, the object is usually to obtain more morphine or sympathy.

"If minimized, i.e., if their suffering is wilfully suppressed, or concealed, the patient's object is usually to effect his discharge sooner. As far as dissembling is concerned, some drug addicts are consummate actors.

"Sometimes, as Light and Torrance mentioned in their article, patients who are in possession of smuggled narcotics will simulate suffering to allay suspicion.

"Symptoms of withdrawal or abstinence may be referred to almost any organ of the body. The psychic symptoms are usually first to appear. The patient becomes restless, uneasy, and fidgety, not remaining very long in one position, i.e., there is increased psychomotor activity of a disagreeable nature. He also shows fear, anxiety, and also some irritability.

"The method of treatment at this stage may either quiet him, or exaggerate his symptoms, or excite him.

"The fact that at this time mere assurance that he will be taken care of, or the giving of a sterile hypodermic will quiet him for quite a while, shows how important the mental factor is in the treatment of these cases.

¹ Am. J. Psychiatry: 10, 488 (1930).

"Soon, within 12 to 24 hours, physical symptoms appear (the 'yen' as addicts call it), and these at times alternate with or are modified, or exaggerated by the psychic element.

"The patients complain of alternate hot or cold flashes, show vasomotor instability, may sweat profusely, or show blushing or erythema of the skin, or pallor and goose flesh. Sometimes the patients appear cyanosed. There may be slight rise of temperature for several days.

"Then a multitude of other symptoms may appear in any number of combinations or degrees of severity.

"There is an apparent increase of many of the bodily secretions; lachrymation, with dilated pupils; coryza, with sneezing and increased bronchial secretion with cough and expectoration, so that the patient complains that he has a 'cold in the head and chest.' There may be yawning, with sighing or dyspnoea, or, only increased rate of respiration.

"The pulse rate may remain unchanged or may show considerable fluctuation, becoming rapid or slow; small, weak, collapsible, thready, intermittent. The patient may complain of anginoid pains. The blood pressure in some conformity with the general vasomotor instability may show fluctuations, and there is often a fall in the systolic and diastolic readings. There may be a slight leucocytosis.

"There may be salivation, with nausea, retching and vomiting, which may become so marked as to be blood-streaked, with terrible, binding, colicky abdominal cramps, and more or less diarrhea. Sometimes the patients may vomit and have involuntary bowel movements simultaneously. The large amount of bile vomited in some cases may be significant. In some cases the patients put their fingers down their throats to induce vomiting when nauseated. Often also they complain of 'heart burn' (pyrosis) with acid eructation. The abdominal cramps, vomiting, etc., may simulate an acute surgical condition.

"With the anorexia, vomiting, inability to retain food or fluids, etc., there is a rapid loss of weight which may vary from a few pounds to twenty or more pounds in a few days. As a result the patients may show rapid emaciation; the change in their appearance may take place so quickly and be so marked as to make them appear to be entirely different individuals. As a result of emaciation and dehydration, etc., there may be marked prostration, sometimes collapse.

"In the genito-urinary system the patients may show a frequency of micturition, occasional albuminuria, or acetonuria; or increased sexual activity with numerous seminal emissions.

"There are very constant painful, spasmodic muscular aches, and twitchings, which, when very marked are called by the patient 'twisters.' There may be generalized fine tremors, simulating those of an alcoholic. Many patients complain of joint pains, and pains in the back (which they call 'kidney trouble').

"In the nervous system the symptoms may be very complex. First, there is a marked sleep disturbance, patients sleep fitfully, at irregular intervals;

often they remain awake all night, sleeping for short periods during the day time. Occasionally there is insomnia for several days.

"There may be headache, disturbance of vision with diplopia, or dimness; and the senses of hearing, smell, or taste may be either impaired, or rendered more acute (the keen sense of hearing of some drug addicts is well known). Occasionally they complain of ringing in the ears.

"There appears to be a generalized hyperesthesia to heat, cold, touch, and painful stimuli; and some scarred veterans of the hypodermic, who had jabbed themselves on innumerable occasions with eye-droppers, safety-pins, horse-shoe nails, and what not, will complain of the prick of a fine hypodermic needle. As they explain it their 'nerves are all on the outside.' Neuralgic pains may manifest themselves anywhere in the body, supra-orbital, facial, dental, intercostal, sciatic, etc. Some patients complain of testicular pain.

"The tendon reflexes are usually increased.

"Some patients may laugh or cry alternately, become hysterical, shout, curse, dash their heads or fists against the wall impulsively, or smash anything within reach. Sometimes they have a real or simulated convulsion or delirium, even a mild transitory psychosis, or mental confusion with impairment of memory. They become slovenly and untidy, expectorate in bed and on the floors. Some show exhibitionism.

"All their psychopathic or psychoneurotic traits become exaggerated and obvious during the withdrawal period. The emotional tone is one of extreme dissatisfaction, and the patients become very capricious in their wants, making all kinds of requests, and often they become very finicky about their food.

"Not every patient suffers all these symptoms. Some go through an abrupt withdrawal with little or no evidence of distress.

"Thus we see that every withdrawal is a test of the addict's resistance and endurance. The suffering and release of nervous energy suppressed for a long time, place a severe tax on all the vital organs and the period of unrest, suffering, and semi-starvation may result in death."

From this complete account it can readily be seen that the withdrawal symptoms suffered in the four cases presented here were not typical in extent, intensity, or duration. When patients were given a seven-day reduction treatment Lambert's Committee found that 8% of the patients suffered severe withdrawal symptoms and 64% had light withdrawal symptoms. There is nothing in the report to indicate that the number of withdrawal symptoms was decreased by the gradual reduction treatment. By comparison with that method of treatment, sodium rhodanate also reduces the suffering upon withdrawal of morphine. Many of the symptoms reported by Lambert have not been observed at all during this study.

From the graph presented on page 512 of Lambert's report, a relationship between the seven-day reduction treatment and the sodium rhodanate treatment can be obtained. The maximum intensity of withdrawal symptoms comes two days after the last dose of morphine, under the seven-day reduction treatment. Whereas, when sodium rhodanate is used the maximum intensity,

ruling out the delirious states that have been observed, comes on the last day that the patient is given morphine. This is shown in Fig. 1. This graph was made largely on the basis of Case 1. Nothing has arisen in the later cases to indicate that it does not represent the picture quite accurately. No attempt was made to evaluate the withdrawal symptoms numerically. Therefore, the ordinal values in Fig. 1 are purely arbitrary. The curves show three important things. In the first place, the withdrawal symptoms did not commence until the sodium rhodanate treatment was more than half through; whereas, in the seven-day withdrawal the symptoms were present throughout. Secondly, the

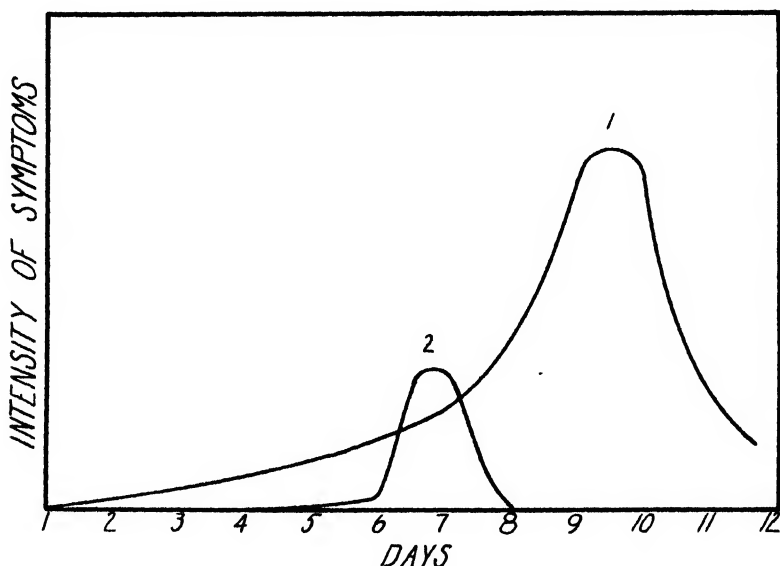


FIG. 1

Curve 1—Seven-day reduction treatment

Curve 2—Treatment with sodium rhodanate during six-day reduction

shift in the maximum of the curve indicates very strongly that sodium rhodanate forces morphine out of the system more rapidly than it would go out normally. In other words, there is a forced period of irritability as a result of the peptizing effect of the rhodanate ion. The third deduction is that the withdrawal symptoms are less intense when sodium rhodanate is used.

It is not amiss to re-state the proposition that the really important problem is not the reduction of discomfort during withdrawal, but rather the mental rehabilitation of the patient. As this report shows, a fair degree of success has been met with along the line of rehabilitation. It seems to be a peculiar twist of the medical mind¹ that it gets all tangled up with the word "specific." It is felt, in some quarters, that for a drug to be of use in drug addiction it must be a specific for that disease. The use of the word almost becomes anthropomorphic. On the other side of the question, there is no real reason why one should

¹ Treadway: Science News Supplement, May 13, 1932.

have to use a drug which goes only to the centers affected by morphine, and acts as an antidote only to the alkaloid. If the nervous system, or part of it, is agglomerated there is no reason whatever why any effective peptizing agent should not be used to treat the condition, provided the drug used neither kills the patient nor causes permanent damage. Searching for a "specific" has been in the past and probably will continue to be rewarded only by the consumption of time. No claim of a miraculous cure has been made, Dr. Treadway's inference notwithstanding.

There are many stumbling blocks in the path to the successful use of sodium rhodanate in the treatment of drug addiction. The first difficulty that is likely to arise is with the purity of the sodium rhodanate. To be on the safe side the salt should be recrystallized from water solution at least once before use. The saturated solution of the drug should be filtered before crystallization is started. *Potassium and sodium rhodanates are not interchangeable, and only the sodium salt should be used.* When administering the peptizing agent *it should be given to effect*, barring only very serious complications. Using very large doses of the drug in many cases in the course of this and other studies in reversible agglomeration and peptization in living tissue, no permanent damage has been done in any case by the sodium rhodanate. Discontinuing the drug can generally be relied upon to remedy any side effects. Because a patient becomes dizzy, nauseated, weak, or exhibits any one of a number of other symptoms is generally no excuse for discontinuing the use of the peptizing agent. Because one does not see an effect is no reason to presume that sufficient dosage will not produce it. That may be poor medical practice; but it is sound scientific procedure. It has been pointed out how psychoses can be handled. There is some danger in using too much sodium rhodanate after withdrawal; and care must be exercised that a condition of over-peptization, such as that which makes some addicts begin the use of morphine, is not produced. If such a state is brought about, agglomerating agents should be employed immediately in order that the patient shall not revert to the use of drugs. Such a case has been observed experimentally, and will be presented in a later paper. Sodium rhodanate should not be used to control weakness. If a great deal of the drug is used, and sleeplessness results, the sleep center is probably over-dispersed; a decrease in the dosage is then indicated. Extreme care, and careful study, in the light of the theory, must be taken in deciding whether to use agglomerating or peptizing agents during the rehabilitation. If the patient was originally over-peptized before taking morphine, sodium amytal will be useful. If the reverse is true, sodium rhodanate or bromide is indicated. There is nothing to be gained at the present time by attempting to apply colloid therapy to anyone who does not desire sincerely to be cured; such is almost surely the case with many prisoners.

Sodium rhodanate should not be used in cases of active or arrested tuberculosis, because it is probable that it will aggravate the condition. Patients suffering from kidney disorders, heart disease, functional or organic, and painful organic diseases should not be given more than five grains of sodium rhodanate a day. Such a small amount is totally useless in the treatment of

drug addiction. In cases of severe hypotension, sodium rhodanate and ephedrine can be used to advantage almost surely. It should be pointed out that sodium rhodanate does not act rapidly and that its maximum peptizing action comes at a high concentration in the body. Therefore, one can not expect good results by starting to give this drug simultaneously with abrupt withdrawal. It is probably inadvisable to use abrupt withdrawal and sodium rhodanate therapy.

The deliria and psychoses that have been observed did not cause particular concern at the time because after a short study it became obvious how to treat them. Naturally it is felt that it is not necessary or desirable to have these two factors as part of the picture. Further study is needed in order to determine how to avoid them.

Despite all of this, the treatment of drug addiction with sodium rhodanate is not yet standardized by any means. It requires a thorough understanding of the theory and principles underlying the treatment and the action of the drug, combined with the determination and courage to go ahead. Skill and practice in the use of sodium rhodanate for various conditions is a necessity. Dr. Treadway¹ reports that his experiences with the use of sodium rhodanate do not parallel those reported in this paper. Despite a request, he has not released information as to exactly what he found, or the procedure followed in making his experiments. It is certain that he was dealing with a different type of case than those reported here. From the very nature of the thing, he could not have duplicated the treatment as used here. Every addict presents a slightly different problem, and the treatment is not yet standardized. There was no sufficiently pure sodium rhodanate on the market, so far as we are aware, at the time that his experiments were made. Until such time as further and more specific information is forthcoming, Dr. Treadway's conclusions will have to be considered as based on bad experimentation. Just where he slipped up can not be stated at the moment.

So far as is known, no two agglomerating drugs, working on the same set of nerves, will produce the same intensity of symptoms in equal doses. In other words, different drugs agglomerate to different degrees. Heroin is approximately three times as strong as morphine; that is, about one-third of the dose produces the same results. The theory of the action of heroin, and the method of treatment of heroin addiction, is the same as for morphine. Yet, it is theoretically possible, and indeed even probable, that sodium rhodanate is not strong enough as a peptizing agent to overcome the withdrawal symptoms when heroin is taken from an addict, either abruptly or gradually. Large doses of sodium rhodanate are necessary to alleviate the abstinence symptoms in morphine withdrawal. Heroin, being stronger than morphine, is a better agglomerating agent. It probably will require correspondingly more sodium rhodanate to relieve the abstinence symptoms of heroin withdrawal.

It seems probable that the safest procedure in the treatment of heroin addicts is to withdraw the heroin and substitute morphine. In carrying this

out enough morphine should be used to prevent the appearance of any withdrawal symptoms. Then, after one or two weeks, when the addict has become thoroughly accustomed to the morphine, the usual sodium rhodanate treatment should be instituted. Even then, larger amounts of sodium rhodanate may be necessary.

Were sodium rhodanate clinically of practically no use at all in the treatment of heroin addicts, it would not affect the theory in the slightest. A case that is entirely analogous has been reported.¹ Sodium amytal and nembutal are both anesthetics of the barbituric acid series. Less nembutal is required to produce anesthesia. Sodium rhodanate exhibits a marked antagonistic action against sodium amytal; but it was a long time before it could be shown that it antagonizes nembutal; and a marked antagonistic action has never been observed. Along the same line veronal is not such a good coagulating agent as morphine; and veronal addiction is easier to treat than morphinism.

Eighty cases of drug addiction were treated with sodium rhodanate in another place. The source of the sodium rhodanate is not known. Because they felt that there was danger connected with the use of large doses of sodium rhodanate, these people did not use much more than five grains of the drug per day during withdrawal. They combined it with ammonium bromide, thus introducing a much weaker peptizing anion and a toxic cation. Five grains of sodium rhodanate daily is not to be expected to produce any visible ameliorating effect on the abstinence symptoms. It is clear where this experiment went wrong.

A doctor reported that upon giving a veronal addict, who was using fifteen grains of the drug a day, five grains of sodium rhodanate daily he became very excited and nervous. The theory is the same as that underlying the treatment of morphinism. It is clear that the doctor only gave enough of the dispersing agent to peptize the agglomerated colloids to the stage of irritability. He should have given about six times as much sodium rhodanate rather than shifting to sodium amytal, another agglomerating agent.

There is one fact that remains to be explained, if the assumption is made that this work is wrong; that fact is that we can treat morphinism successfully.

Four more cases of morphinism that have been treated by this method will be reported shortly.

The general conclusions to be drawn from this paper are:

1. A review of the theories of drug addiction reveals that they do not account for the facts met with; and do not give a rationale for the action of habit forming drugs upon which to base a proper treatment.
2. A review of the various methods for the treatment of drug addiction shows that, aside from the methods used by Poppe and by MacLeod, there is no satisfactory drug to combat withdrawal symptoms.
3. The problem of rehabilitation is the only important one that has to be faced. The literature shows that the surface has only barely been scratched.

¹ Bancroft and Rutzler: *J. Phys. Chem.*, **35**, 1185, 3036 (1931).

4. Combining Abe's ideas with the theory of reversible agglomeration in living tissue, a useful theory of drug addiction and its treatment has been evolved.

5. The new theory accounts for the facts of drug addiction, withdrawal, tolerance, and rehabilitation.

6. Since by the theory morphine causes agglomeration of certain of the protein colloids of the nervous systems, peptization with sodium rhodanate should be a useful method for treating drug addicts.

7. Four cases of morphinism were treated using large amounts of sodium rhodanate. Laboratory, clinical, and psychological data are presented which show the various reactions of the patients.

8. Sodium rhodanate, when used properly, alleviates withdrawal symptoms.

9. Delirium resulted in 75% of the cases at the end of the withdrawal period.

10. Transient psychoses developed in two cases. Colloid therapy straightened one case out, and endocrine therapy the other.

11. Mental rehabilitation was accomplished, on the basis of the theory, in 75% of the cases. One case was a "pathological thrill-seeker" and was discharged using morphine.

12. The new treatment of drug addiction has not been standardized.

13. Some morphine addicts exhibit paranoid symptoms which are due to agglomeration.

14. There are many pitfalls in the reduction of the theory to practice. These are discussed. Illustrations of how some of them are surmounted from the point of view of the theory are given.

15. Intelligent application of the theory makes it possible to use large amounts of sodium rhodanate and accomplish the successful treatment of morphinism. Despite the statements of some medical men, pure sodium rhodanate is not toxic in doses up to 90 grains in a day.

16. Morphinism is a disease.

17. Sodium rhodanate forces morphine out of the body more rapidly than if no medication were used.

18. Much progress has been made; but much work remains to be done.

19. The conclusions drawn by the United States Public Health Service are undoubtedly based on bad experimentation, though the actual mistakes cannot be pointed out until the details of those experiments have been released.

20. The treatment of heroin addicts can probably be accomplished best by substituting morphine for the heroin, and then withdrawing the morphine with the aid of sodium rhodanate.

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SULPHATES OF MERCURY AND STANDARD CELLS

BY R. B. ELLIOTT AND G. A. HULETT

A most important stage in the development of our standards of electromotive force was the introduction of mercurous sulphate as a depolarizer. The unique properties of this salt have made our standard cells possible. It is a mercurous salt with a rather small solubility (about a gram in a liter) so that diffusion from the cathode system is not excessive, while the solubility is sufficient to give a rather large potential at a mercury electrode. Some 90% of the E.M.F. of the cadmium cell is at the cathode.¹ Now this cathode potential depends upon the ability of the mercurous sulphate depolarizer to establish and maintain a very precise concentration of mercury ions at the mercury electrode, so that the reproducibility and constancy of standard cells depends on this property of mercurous sulphate, and obviously the chemical and physical properties of mercurous sulphate are the important factors. Any factor that has a bearing on the mercury concentration resulting from a given preparation of mercurous sulphate is important from the standard cell standpoint. Any impurities are to be feared, especially any other mercury salts present as a result of adsorption or isomorphism. Also it is well known that solubility varies with the size of the particles of the solid.² When the electrolytic method of preparing mercurous sulphate was developed it was found that when the product was stirred with electrolyte to become sufficiently coarse-grained so that it settled rapidly, that this product showed no measurable effect due to surface tension. Later von Steinwehr³ attempted to explain the variations of standard cells as due to size of particle of the depolarizer.

Now, a product that is obtained as well-formed crystals with reflecting surfaces is less subject to these chemical and physical defects. Consequently, considerable attention has been given to obtaining a well crystallized preparation of mercurous sulphate. Both the chemical and electrochemical method of preparing mercurous sulphate give products of good particle size which appear to be crystalline, but a microscopic examination reveals no reflecting crystalline surface but a rather rough crust-like aspect that by no means excludes adsorption or surface tension effects.

Gardiner and Summers⁴ took advantage of the difference in solubility of mercurous sulphate in 1.5 molar sulphuric at 100° and 20° and by a hot-cold circulation method, succeeded in obtaining some sizable water-clear crystals with perfectly reflecting surfaces. The yield was not satisfactory so we have pursued the problem further. Mercuric sulphate is readily reduced by SO₂

¹ Int. Electrical Congress, St. Louis, 2, 113 (1904).

² Surface tension effect, Hulett: *Z. physik. Chem.*, 37, 385 (1901).

³ *Z. Instrumentenkunde*, 20, 205 (1905).

⁴ *Trans. Am. Electrochem. Soc.*, 56, 143 (1929).

or mercury and the products give perfectly normal values to cells in which they are used as depolarizers. It was thought that by bubbling air-diluted SO_2 through an acid solution of mercuric sulphate that it might be slowly reduced and give a crystalline product but no matter how much the SO_2 was diluted the mercurous sulphate appeared as a fine-grained precipitate.

Now experience shows that most satisfactory crystals appear in quiet solutions where slow diffusion brings the reagents together, so it seemed possible that by allowing SO_2 to slowly diffuse into an acid solution of mercuric sulphate our objective might be attained. A solution of mercuric sulphate was placed in a deep crystallizing dish and in this was placed a bottle partly filled with dilute SO_2 solution and all covered with a glass plate with the idea that the SO_2 would diffuse out of the bottle slowly and reduce the mercuric sulphate. The diffusion was too rapid and the undesired precipitate appeared. Therefore, the bottle was removed from the crystallizing dish and connected to the upper part of the dish through a long tube with a stopcock. By this means it was possible to so restrict the flow of SO_2 that definite crystals appeared and grew on the bottom of the dish. The solution was about 1 cm. deep. Now it was desirable to use the SO_2 direct from a cylinder of the liquid with a pressure of some 4 to 5 atms. By using a very fine capillary, the flow was sufficiently retarded. A piece of 6 mm. thermometer tubing was softened in the flame and drawn down to a capillary about .3 mm. in diameter with a calculated internal diameter of only .013 mm. Some $1\frac{1}{2}$ meter lengths of this capillary joined to the liquid SO_2 cylinder restricted the flow of the SO_2 satisfactorily so that brilliant crystals formed on the bottom of the crystallizing dish. By adjusting the length of the capillary a desirable variation in the rate was attained and by leading the SO_2 into 0.1 normal iodine solution the rate of flow was determined. With a 30 cm. crystallizing dish satisfactory crystals were obtained when the capillary delivered SO_2 into the upper part of the dish at a rate of 200 cu. mm. (0.2 cm.³) a second, while with a rate of .77 cm.³ per second, a precipitate was formed in the mercuric sulphate solution.

Clear crystals with dimensions of $1\frac{1}{2}$ to 1 mm. were readily grown. These were very brilliant crystals indicating a high refractive index. Some of this product turned slightly yellowish in contact with a neutral cadmium sulphate solution. On carefully examining the crystals they were seen to be made up of two types, little plates and cubes. On separating them it was found that the plates were pure mercurous sulphate, while the cubes turned yellow in neutral electrolyte and proved to be mercuric sulphate.

The product had been obtained from a 1 to 6 sulphuric acid saturated with mercuric sulphate and it seemed that some mercuric salt crystallized from this solution as the mercuric was reduced to the less soluble mercurous sulphate and crystallized. With a solution only 75% saturated with mercuric in the crystallizing dish, diffusion of SO_2 yielded only plates and it appears that a 50% saturated solution is quite satisfactory. 150 grams of mercuric sulphate in a liter of 1 to 6 sulphuric acid is quite safe, as only plates of pure mercurous sulphate crystallize from such a solution and these plates may be

thoroughly washed with dilute sulphuric acid to remove every trace of the electrolyte and crystallized mercuric sulphate. These crystals may be washed with alcohol and ether and dried and may then be used directly in cells.

Some of these crystals have been analyzed by a method developed in this laboratory.¹ A platinum crucible was amalgamated internally and the crystals weighed in, then covered with distilled water and with a platinum spiral anode above the crystal. A current of .01 amperes deposited the mercury as fast as the crystals dissolved, liberating the acid. When the mercury was all deposited the acid was syphoned off, water being added simultaneously, so that when milliammeter showed zero reading the deposit was completely washed. The last wash water was removed and the crucible and deposit dried in a vacuum desiccator, and the mercury weighed directly, while the acid was titrated with 0.1 N NaOH solution.

The sum of the weights of mercury and mass of SO_4 titrated gave a check on the weight of crystals used.

Two analyses gave as the ratio of mercury to SO_4 , 2.009 to 1 and 2.010 to 1, so that the plates are Hg_2SO_4 and an exceptionally pure product and the behavior of this product as a depolarizer in cells is of interest. A typical cadmium and zinc cell gave the following record at 25.00:—

Time after construction	Saturated cadmium cell	Saturated zinc cell
1 day	1.018419 v.	1.420244 v.
1 week	1.018281 v.	1.420200 v.
2 weeks	1.018261 v.	1.420197 v.
7 weeks	1.018234 v.	1.420201 v.

Gardiner and Summers² were successful in preparing some water-clear sizable crystals of mercurous sulphate by crystallization from 1.5 molar sulphuric acid, by a hot-cold circulation method. These were exceptionally well formed crystals with reflecting surfaces, but since these crystals gave a higher value to the cadmium cell than did the gray electrolytic mercurous sulphate, this gray electrolytic has been taken as the standard on account of its reproducibility and excellent record in standard cells. There is certainly some difference between the electromotive properties of the two products, and one would be inclined to regard the well crystallized product as giving the "normal value." Certain it is that the crystals are quite free of surface tension effects on the solubility. If this were a factor we would find the electrolytic giving the greater concentration of mercury in the electrolyte and so the greater E.M.F. to the cell but just the opposite is observed. Therefore such an explanation is untenable.

Aside from crystalline differences there is much finely divided mercury on the surfaces of the electrolytic product and this may well be a factor.

¹ Perdue and Hulett: J. Phys. Chem., 15, 147 (1911).

² Trans. Am. Electrochem. Soc., 56, 143 (1929).

Now if the crystals are brought into a dilute sulphuric acid solution of SO_2 they are at once covered with a grey coat of finely divided mercury globules, so it is a simple matter to add this factor of finely divided mercury to crystals of mercurous sulphate. It is only necessary to wash the crystals on the filter with a dilute acid solution of SO_2 . They turn grey and with continued washing the product may be made to appear quite black. Crystals of mercurous sulphate treated as just indicated have been used for the depolarizer of standard cells with the following results:

Time after construction	Saturated cadmium cell	Saturated zinc cell
1 day	1.016840	1.41975
1 week	1.017924	1.420108
2 weeks	—	1.420174
7 weeks	1.018105	1.420203

Obviously finely divided mercury plays an important rôle in the depolarizer of standard cells and calls for a careful study from the practical and theoretical standpoints.

THE HYDROGEN ION CONCENTRATION OF FERRIC HYDROXIDE SOLS

BY WINIFRED L. McCLATCHIE

Although a number of the more common sols of the suspensoid type have been extensively studied, the problem of accurately deducing their constitution is far from completely solved. A critical examination of the literature reveals many serious discrepancies, not the least of which is in the hydrogen ion concentrations determined by different methods with otherwise similar sols. For example, Browne,¹ using a hydrogen electrode directly in a ferric hydroxide sol, found a hydrogen ion concentration of 3×10^{-7} N for a sol comparable in the concentration of iron and chlorine and in electrical conductivity to one for which Wintgen and Biltz² report a concentration of 3.8×10^{-4} N on the basis of hydrogen electrode measurements with the ultrafiltrate.

Reliable values for the hydrogen ion concentrations of sols of metallic oxides and hydroxides are especially important in deducing the constitutions of these sols, for hydrogen ion is both the principal electrolytic cation and a part of the hydrolytic equilibrium, hydroxide + acid \rightleftharpoons basic salt + water, that is presumably responsible for the stabilizing agent of many of these sols.

Many methods have been used for evaluating these hydrogen ion concentrations, but no one has subjected the methods to a critical comparison, so that there is no reliable basis for evaluating the existing data, or of accounting for the discrepancies therein. The object of this investigation with ferric hydroxide sols was twofold. It was desired to compare the results obtained by several of the more common methods, in hopes that this might help to explain some of the present discrepancies. The principal object, however, was to establish a reliable method for such determinations, and to use the hydrogen ion concentrations thus obtained in conjunction with other physical and chemical data to deduce the constitution of these sols.

Ferric hydroxide sols were considered to be most suitable for the investigation, for they have been the subject of extensive study, their chemical constitution is well established, they have been found to remain stable over a long period of time,³ and their electrical properties are fairly constant with time.⁴

Experimental

Preparation of Sols. Sols for this work were prepared by neutralizing ferric chloride solutions with aqueous ammonia. The required amount of ferric chloride was dissolved in distilled water, the solution was cooled to

¹ F. L. Browne: J. Am. Chem. Soc., **45**, 297 (1923).

² R. Wintgen and M. Biltz: Z. physik. Chem., **107**, 403 (1923).

³ J. Böhm: Z. anorg. Chem., **149**, 203 (1925).

⁴ R. Wintgen and M. Biltz: Z. physik. Chem., **107**, 403 (1923).

about 10°, and an approximately 12 per cent solution of ammonia was added dropwise, with mechanical stirring, until the amount added was equivalent to 60 to 70 per cent of the iron. The ammonia solution was prepared by redistilling the stock reagent. Three sols were prepared by this method, ferric chloride solutions of the following concentrations being used: for sol 3, 600 g. of Sterling's C. P. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 4.5 liters of water; for sol 13, 500 g. of Kahlbaum's $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ "for analysis" in 2 liters of water; and for sol 20, 800 g. of Merck's $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ "free from phosphorus" in 3.5 liters of water.

These sols were purified by dialysis for several weeks against continuously changing boiled-out distilled water with a specific conductivity of 1.5 to 2.5×10^{-6} . The water was boiled in interconnected flasks, from which it passed into a large flask in which cellophane tubes containing the sol were suspended. All glass was Pyrex. Air entered the system only through wash bottles of 50 per cent sodium hydroxide and boiled-out distilled water.

The removal of carbon dioxide was considered important in view of the work of Freundlich and Wosnessensky¹ who showed that carbonate ion can serve as the stabilizing agent for ferric hydroxide sols, and it was thought possible that it might tend to replace chloride ion.

Soft glass was used in the apparatus for the dialysis of sol 3, and the water showed a pH of 8.5 and a specific conductivity of about 1.5×10^{-5} . Experiments with this sol are therefore of only secondary value.

All sols were stored in Pyrex containers equipped with inlet and outlet tubes, which were kept closed except for the removal of samples.

Chemical Analysis of Sols. The sols were analyzed for iron and chlorine, both determinations being made on the same sample. The ferric hydroxide was dissolved by warming with concentrated sulfuric acid, and a double precipitation of iron was made. Iron was determined as ferric oxide, and the combined filtrates from each sample were used for the determination of chlorine as silver chloride. Each value in the second, third, and fourth columns of Table I represents the average of at least two determinations.

TABLE I

Iron and Chlorine Concentrations of the Sols and the Specific Electrical Conductivities at $25^\circ \pm 0.02^\circ\text{C}$

Sol	Gram atoms of Fe per 1000 g. H_2O	Gram atoms of Cl per 1000 g. H_2O	Gram atoms Fe Gram atoms Cl	$\text{K} \times 10^4$
3	0.1797	0.02242	8.02	3.287
13	0.3073	0.04450	6.91	5.695
20	0.274	0.0379	7.7	4.190

Electrical Conductivity. The electrical conductivities of these sols were measured by a simple Wheatstone bridge method. The sols were allowed to stand for at least two months before final measurements were made, for it has been shown that their conductivity becomes practically constant within this time.² The electrical conductivities obtained are given in column 5 of Table I.

¹ H. Freundlich and S. Wosnessensky: *Kolloid-Z.*, **33**, 222 (1923).

² R. Wintgen and M. Biltz: *Z. physik. Chem.*, **107**, 403 (1923).

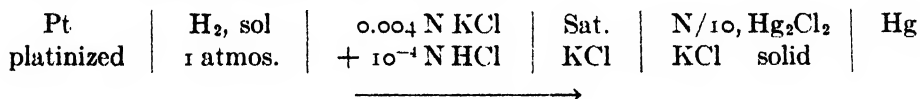
Hydrogen Ion Concentrations

The hydrogen ion concentrations of the sols were determined directly by means of the hydrogen, quinhydrone, and glass electrodes; and in the ultra-filtrate by means of the glass electrode.

A. *Measurements with the hydrogen electrode.* Hydrogen electrode measurements were made by a method similar to that of Browne,¹ and of Pauli and Matula.² Sol 3, with which the measurements were made, had a ratio of gram atoms of iron to gram atoms of chlorine of 8, and, according to Browne, a stable equilibrium can be obtained with all sols for which the ratio is greater than 5.

A cell of Pyrex with lightly platinized platinum wire electrodes was used. The electrodes were replatinized after each measurement with the sol. Hydrogen was supplied from a cylinder and was passed through solutions of mercuric chloride, silver nitrate, alkaline pyrogallol, alkaline permanganate, and distilled water. A dilute bridge solution containing simultaneously approximately 0.0039 N potassium chloride and 10^{-4} N hydrochloric acid was used.

The cells measured may be written as follows, the arrow indicating the direction of positive current within the cell:



The difference in potential was measured by means of a type K Leeds and Northrup potentiometer with a high resistance, high sensitivity galvanometer.

Electrodes were used with the sol only when they had given stable potentials with potassium acid phthalate solution. In a number of cases erratic results were obtained, or there was no approach to equilibrium in 60 to 90 minutes. The determinations in which equilibrium appeared to have been attained are summarized in Table II, where E is the observed electromotive force of the cell and C_{H^+} is the corresponding activity of hydrogen ion.

TABLE II
Hydrogen Electrode Measurements

Time in minutes to attain equilibrium	E	pH	$C_{H^+} \times 10^5$
30	0.628	5.03	0.93
40	0.620	4.92	1.20
40	0.639	5.22	0.60
10	0.623	4.95	1.12
60	0.655	5.53	0.20

¹ F. L. Browne: J. Am. Chem. Soc., 45, 297 (1923).

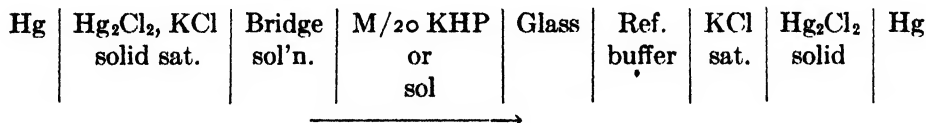
² W. Pauli and J. Matula: Kolloid-Z., 21, 49 (1917).

These results lead to the same conclusions that have been drawn by other experimenters;¹ namely, that equilibrium is difficult to attain, and that the results are not reliable. This is not surprising, for a system containing even traces of ferric ion would show an oxidation reduction potential that would vary with the degree of reduction. There is also the possibility of flocculation of the colloid by the gas bubbles.²

B. Measurements with the glass electrode. Of all of the methods that have been used with ferric hydroxide sols, the glass electrode was considered to be the most promising for reliable results. It eliminates most of the difficulties associated with the hydrogen electrode, such as oxidation reduction potentials and flocculation by gas bubbles. The only serious uncertainty is the liquid junction potential between the sol and bridge solution, which is necessarily present in any electrometric determination of a single ion activity.

Two methods for measuring the electromotive force of the cells were used. The first was that described by Kerridge,³ a Lindemann electrometer being used as null point instrument in conjunction with a type K potentiometer. The second method was that of Robertson,⁴ for which a high resistance, high sensitivity galvanometer was substituted for the electrometer of the previous method. It was sensitive to less than one millivolt with electrode resistances under ten megohms.

Each electrode was standardized against M/20 potassium acid phthalate buffer, with an approximately neutral reference buffer, and a saturated potassium chloride bridge. The cells measured may be written as follows:



The results obtained are summarized in Table III. E_{sol} is the total electromotive force of the cell with the sol, and E_{KHP} is that with M/20 potassium acid phthalate. The KCl, HCl bridge was the same as that used with the hydrogen electrode.

Glass electrode measurements were also made with several samples of ultrafiltrate. The sol was filtered through a cellophane membrane by means of a high pressure apparatus, the details of which will be described in a subsequent communication. The hydrogen ion concentrations depend upon the conditions of ultrafiltration, as will be explained in discussing the significance of the results of ultrafiltration. This method is therefore an uncertain means of finding such values for the sols. The range of results is given in Table V.

¹ R. Wintgen and M. Biltz: *Z. physik. Chem.*, **107**, 403 (1923); A. W. Thomas and A. Frieden: *J. Am. Chem. Soc.*, **45**, 2522 (1923).

² H. M. Stark: *J. Am. Chem. Soc.*, **52**, 2730 (1930).

³ P. T. Kerridge: *Biochem. J.*, **19**, 611 (1925).

⁴ G. R. Robertson: *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).

TABLE III

Glass Electrode Measurements

Sol	Bridge	E_{sol}	E_{KHP}	T°	pH	$C_{H^+} \times 10^5$
3	N/10 KCl	0.154	0.171	21	4.26	5.5
3		0.151	0.171	21	4.31	4.9
3		0.146	0.163	18	4.26	5.5
3		0.146	0.163	18	4.26	5.5
3	KCl— HCl	0.1407	0.1310	21	4.14	7.2
3		0.1402	0.1310	21	4.14	7.2
13	N/10 KCl	0.145	0.164	20	4.30	5.0
13		0.146	0.164	20	4.28	5.2
13		0.144	0.163	17	4.30	5.0
13		0.140	0.163	17	4.37	4.3
13		0.142	0.163	17	4.33	4.7
13	KCl— HCl	0.1327	0.1310	21	4.00	10.0
13		0.1325	0.1310	21	4.00	10.0
20	KCl— HCl	0.1550	0.1310	21	4.38	4.2
20		0.1520	0.1300	20	4.35	4.5

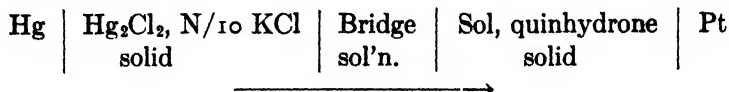
TABLE IV

Quinhydrone Electrode Measurements

Sol	Bridge	E	T	pH	$C_{H^+} \times 10^5$
3	KCl, HCl	0.1270*	20	4.16	6.9
		0.1271	20	4.16	6.9
3	Sat. KCl	0.1145	23	4.18	6.6
3	N/100 KCl	0.1182	23	4.12	7.6
		0.1170	23	4.13	7.4
3	N/500 KCl	0.1220	23	4.05	8.9
13	KCl, HCl	0.1329*	20	4.06	8.7
		0.1335	20	4.05	8.9
20	Sat. KCl	0.0980	24	4.43	3.7
		0.0975	24	4.44	3.6
20	N/100 KCl	0.1061	24	4.30	5.0
		0.1062	24	4.30	5.0
		0.1064	24	4.29	5.1
20	N/500 KCl	0.1193	24	4.07	8.5
		0.1173	24	4.19	8.0

* This calomel half cell showed an E.M.F. of 0.3345 V. In all others it was 0.3410 V

C. Measurements with the quinhydrone electrode. The quinhydrone electrode, in conjunction with various bridge solutions, was used with the same potentiometric set up as was the hydrogen electrode. With saturated potassium chloride, which was more dense than the sol, the siphon leading from the electrode compartment was filled with sol, which prevented mechanical mixing, and also coagulation in the region of the electrode, the latter occurrence having been found radically to alter the readings. The calomel half cell was checked against an M/20 potassium acid phthalate buffer. The cells measured may be written as follows:



Discussion of Results

The following is a comparison of the values that were considered to be the most reliable by the various methods used.

TABLE V
Summary of Results of Hydrogen Ion Determinations

Electrode	Bridge	Age in weeks	pH	$C_{H^+} \times 10^5$
Sol 3				
Glass	N/10 KCl	28	4.26	5.5
"	KCl, HCl	42	4.14	7.2
Quinhydrone	Sat. KCl	61	4.18	6.6
"	N/100 KCl	61	4.12	7.5
"	N/500 KCl	61	4.05	8.9
"	KCl, HCl	33	4.16	6.9
Hydrogen	KCl, HCl	30	5.66 to 4.92	0.22 to 1.20
Sol 13				
Glass	N/10 KCl	21	4.30	5.0
"	KCl, HCl	35	4.00	10.0
Quinhydrone	KCl, HCl	26	4.05	8.9
Sol 20				
Glass	KCl, HCl	7	4.37	4.3
Quinhydrone	Sat. KCl	28	4.43	3.7
"	N/100 KCl	28	4.30	5.0
"	N/500 KCl	28	4.08	8.2
Ultrafiltrate from Sol 13				
Glass	N/10 KCl			2.8 to 8.4

An examination of these results shows that the glass and quinhydrone electrodes agree fairly well when used with the same bridge solution and with sols of the same age. The hydrogen electrode, however, although used with the same bridge solution, indicated a concentration of only from one-fifth to one-thirtieth of that shown by the other methods. It may, therefore, be concluded that the glass and quinhydrone electrodes give a true measure of the hydrogen ion concentration of ferric hydroxide sols, and that the hydrogen electrode gives values that are erroneous and much too low.

The effect of different concentrations of bridge solution is shown by the quinhydrone electrode determinations. The differences in hydrogen ion concentration may be seen from Table V and in terms of electromotive forces are shown by the following values:

Sol	$E_{\text{sat. KCl}} - E_{N/100 \text{ KCl}}$	$E_{\text{sat. KCl}} - E_{N/500 \text{ KCl}}$
3	0.0030	0.0075
20	0.0085	0.0205

In general, an increase in the concentration of the potassium chloride bridge solution decreases the apparent concentration of hydrogen ion; and there is no discontinuity in this effect when flocculation of the sol occurs so long as the sol in the region of the electrode is unaffected. It, therefore, seems probable that concentrated potassium chloride bridge solutions give the more nearly correct results, as is the case with simple electrolytes, for they more nearly eliminate diffusion potential, and there is no evidence of a membrane potential due to flocculated colloid.

It has already been pointed out that the hydrogen ion concentrations previously recorded for ferric hydroxide sols, determined by various methods, show wide and inconsistent differences. Several investigators have used these values as a basis for deducing the constitution of the sols studied, and a critical examination of their methods and results is essential in evaluating their conclusions. This is especially true of much of the work of Pauli and his associates, who use such determinations as part of their evidence for classing ferric hydroxide sols as polyvalent strong electrolytes. Pauli and Matula,¹ by use of the hydrogen electrode in the sol, obtained about 8×10^{-6} N; Pauli and Walter,² by means of the hydrogen electrode in the flocculation filtrate, found it to be 3×10^{-6} N; and Kühnl and Pauli³ used a microtitration method to obtain 3.6×10^{-4} N.

It has already been shown that the first method gives low results, and there is no reason to assume that the flocculation filtrate would be identical with the dispersion medium of a sol, and results in this paper show that trustworthy measurements could not be made if coagulation occurred near the electrodes. It is also to be expected that titration would alter the hydrolytic equilibrium of a sol, and results by this method were higher than would

¹ W. Pauli and J. Matula: *Kolloid-Z.*, **21**, 49 (1917).

² W. Pauli and G. Walter: *Kolloidchem. Beihefte*, **17**, 256 (1923).

³ N. Kühnl and W. Pauli: *Kolloidchem. Beihefte*, **20**, 319 (1925).

be predicted by comparison with sols 13 and 20 of this paper. It must, therefore, be concluded that the hydrogen ion determinations used by Pauli and his collaborators are not to be depended upon, but must be replaced by the much higher acidities here shown to be found with glass and quinhydrone electrodes.

Summary

Apparent hydrogen ion concentrations as given by hydrogen, glass, and quinhydrone electrodes have been compared, using sols of ferric hydroxide prepared with special precautions to avoid impurities and of known chemical composition and electrical conductivity. Results with glass and quinhydrone electrodes agree, but hydrogen electrodes give very low and erroneous results.

From experiments with various concentrations and acidities of the bridge solutions it was concluded that concentrated solutions of potassium chloride give the most nearly correct results, especially since flocculation of the sol has no effect so long as it does not occur in the neighborhood of the electrode.

My cordial thanks are due to Professor James W. McBain at whose suggestion this work was carried out.

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THE HYDROLYSIS OF MERCUROUS SULPHATE

BY O. B. HAGER AND G. A. HULETT

The unique properties of mercurous sulphate have made our standards of electromotive force possible, since one may employ mercury and a liquid amalgam for electrodes and a saturated salt solution for the electrolyte, in which mercurous sulphate is sufficiently soluble to give good depolarization.

The only defect so far encountered is the tendency of mercurous sulphate to hydrolyze in aqueous solution. The salt is a combination of a weak base and a strong acid with a pronounced tendency to hydrolyze but this tendency is counteracted by sulphuric acid and by some sulphates in solution. There appears to be no hydrolysis of mercurous sulphate in a saturated zinc sulphate solution, but it does measurably hydrolyze in a neutral cadmium sulphate solution. This fact leads to some important differences between the zinc cell, and cadmium cell and the Weston (unsaturated cell).

The first important information on the hydrolysis of mercurous sulphate was obtained by Gouy.¹ Gouy agitated 10 grams of normal mercurous sulphate with 500 cc. of water at room temperature ($\pm 20^\circ$) until saturation was attained when the solution was removed and a fresh 500 cc. portion of water added, etc. The successive solutions were alike. Gouy analyzed them by removing the mercury electrolytically and then titrating the sulphuric acid. He found a liter of the solution to contain 400 mg. of mercury and the solution from which the mercury had been removed showed, on titration, 160 mg. of SO_3 to the liter. The eleventh 500 cc. portion showed a lower concentration of Hg and SO_3 . Subsequent portions decreased in concentrations until the fourteenth portion, showing only small concentrations. Subsequent portions showed this same small concentration.

Gouy's experiments give a quite clear picture of the hydrolysis of mercurous sulphate by water. The first eleven portions were saturated with respect to mercurous sulphate with an increasing amount of basic sulphate present, and after the fourteenth treatment only the basic salt was present. Gouy observed this residue to be yellow-green and on analysis he arrived at the formula $\text{Hg}_2(\text{OH})_2\text{Hg}_2\text{SO}_4$. The next important contribution was by Cox² from Abegg's laboratory. Cox used Gouy's data in a phase rule diagram and was able to show that between the normal mercurous sulphate and mercurous oxide there is evidence of only one basic salt. Of the composition described by Gouy, Cox also concluded that .002 molar sulphuric acid inhibits the hydrolysis of mercurous sulphate. On page 18 (*loc. cit.*) Cox gives .0041 normal equivalent as the acidity which inhibits hydrolysis but there appears to be an error due to a misinterpretation of Gouy's data. Cox con-

¹ *Compt. rend.*, **130**, 1400 (1900).

² *Z. anorg. Chem.*, **28**, 361 (1901); **40**, 180 (1904).

cluded that the first eleven solutions obtained by Gouy had an acidity of .002 molar sulphuric acid. Gouy analyzed these solutions by removing the mercury electrolytically and then titrating the exhausted electrolyte and found .002 moles of sulphuric acid in a liter. But part of this acid was associated with the mercury which had been removed electrolytically so that the acidity of the original solution, the "equilibrium water" was not that finally titrated but only half that or .001 molar sulphuric acid.

We have obtained a check on this value. On bringing the system mercurous sulphate-water and mercury to equilibrium at 25° it was found that the equilibrium water contained .002 moles of HgHSO_4 in a liter which is an acidity of .001 molar sulphuric acid or .002 normal equivalent. Writers who have followed Cox and assumed that .002 moles of sulphuric acid inhibit the hydrolysis of mercurous sulphate should now defend the proposition that .001 molar sulphuric acid inhibits the hydrolysis of mercurous sulphate. The equilibrium water .002 molar HgHSO_4 will neither dissolve nor hydrolyse mercurous sulphate, but it does not follow that water with .001 moles of H_2SO_4 to the liter will also inhibit this hydrolysis. We have evidence to show that a very much greater acidity is needed.¹

By determining the solubility of mercurous sulphate in sulphuric acid of varying concentrations one finds a break in this solubility curve, at the acidity at which the basic salt appears as a phase. Starting with a strong acid, e.g., $4 \times$ molecular H_2SO_4 where there is no suggestion of hydrolysis, the solubility of mercurous sulphate is quite small, .00087 moles Hg_2SO_4 in a liter. On diluting the acid the solubility increases quite rapidly to .002208 moles in a liter at molecular acidity. Here the curve takes a sharp downward trend uniformly to an acidity of 0.27 moles H_2SO_4 in a liter. At this point there is a slight inflection in the curve as it decreases less rapidly from here on to a minimum value at about .025 molar acidity. Henceforth there is a slow increase in the solubility of mercurous sulphate in distilled water where the hydrolysis furnishes an acidity of .001 molar sulphuric acid and here the experimental curve necessarily ends. The slight inflections in the curve at 0.27 and .025 molar acidities may be connected with a change in the heats of solution at these points. There is no evidence of the appearance or disappearance of a phase at either of these points, while at the sharp break at molecular acidity there is a marked change in the solid phase. Above molecular acidity analysis of the solid phase has shown normal mercurous sulphate while below molecular acidity analysis of the solid phase shows the presence of basic sulphate. Furthermore, the behavior of these products as depolarizers in standard cells confirms these conclusions.

These facts have led to the conclusion that in order to prepare normal mercurous sulphate one must have present at least molecular acidity of sulphuric acid. The curve (loc. cit.) clearly leads to the conclusion that mercurous sulphate may hydrolyse in sulphuric acids of less than molar concentrations.

¹ Int. Electrical Congress, St. Louis, 2, 115 (1904).

We have attempted to test this conclusion by treating normal mercurous sulphate with a large excess of 0.1 molar sulphuric acid, which is 100 times greater acidity than is claimed to inhibit the hydrolysis of mercurous sulphate. Ten grams of chemically prepared normal mercurous sulphate¹ were washed with 0.1 molar sulphuric acid and brought together with 500 grams of mercury and some 1000 cc. of 0.1002 molar acid into a large rotating tube and brought to equilibrium at 25°. 800 cc. of the clear solution was now removed and replaced with an equal volume of the 0.1 molar acid. Successive portions showed the same concentration of mercury but after thirty changes of the electrolyte an accident interrupted the experiment, but the contents of the tube were intact and satisfactorily recovered and enough of the residue obtained for analysis and for filling a cadmium cell.

We have developed a very precise method for determining metals electrolytically² and this method is particularly satisfactory for determining mercury in the rather insoluble sulphate and basic salts. A platinum crucible was amalgamated internally, vacuum desiccated, weighed, and the salt weighed into the crucible. 10 cc. of water was added and a small platinum anode placed just above the salt permitted the mercury to be deposited on the amalgamated platinum as fast as the salt dissolved, leaving the acid in solution. About .010 amp. current served for this purpose. When the salt had disappeared and the mercury had all been deposited with the current left on, the sulphuric acid was syphoned into a little flask, water being simultaneously added until the milliammeter showed zero reading, indicating the complete washing of the deposit. The last of the wash water was removed by a pipette and added to the acid which was titrated by a carefully standardized 0.1 normal NaOH solution, thus giving the SO₄ of the salt taken. The crucible was placed in a vacuum desiccator where it soon dried and was ready to weigh, giving directly the mercury of the sample of salt taken.

Experiments have shown that the weights of these amalgamated and vacuum-dried crucibles are very precise and reliable. The solubility of platinum in mercury is so small that no damage to a crucible results. The process is direct and most satisfactory for these mercury salts. The residue from the above rotation experiment was washed with alcohol and ether, dried in a vacuum desiccator, and 0.4011 grams weighed into the amalgamated crucible on electrolysis this salt was found to yield .3259 g. of mercury, while the acid syphoned off was titrated and required 14.27 cc. of 0.1096 normal NaOH. This gave a calculated .0751 grams of SO₄. Now .4011 g. of normal mercurous sulphate should give .3226 g. of mercury and .07856 g. of SO₄ so that the residue had lost relatively more acid than base by the action of the 0.1 molar sulphuric acid, that is, the salt had been partly hydrolyzed. Some of the residue from the rotation tube was now used for the depolarizer of a cadmium cell which was filled on September 7, 1931 according to the procedure in this

¹ Int. Electrical Congress, St. Louis, 2, 126 (1904).

² Perdue and Hulett: J. Phys. Chem., 15, 147 (1911).

laboratory.¹ But it was not possible to get a reading at 25° until October 26, when it was 1.01685. The following observations have been made by Mr. R. B. Elliott:

September	7 1.01878 (extrapolated)	February	9 1.01501
October	26 1.01685	February	15 1.01482
November	18 1.01601	March	8 1.01458
December	16 1.01563	April	2 1.01443
January	18 1.01544	May	2 1.01408
February	3 1.01502	June	4 1.01374

The initial value is an extrapolated value but the first part of the decrease is nearly linear, so this must be a quite reliable value. At present the rate of decrease is diminishing and probably will continue to do so. But the initial high value and subsequent decrease are quite characteristic of depolarizers that carry basic salt. There appears to be no doubt that normal mercurous sulphate may be so altered by 0.1 molecular sulphuric acid that it gives a high and inconstant value to the cadmium cell when used as a depolarizer. This is quite in line with previous experience. It was found² that mixtures of normal and basic salt always gave a high initial value to cells followed by a decrease and it also developed that a mercurous sulphate which had been partially hydrolyzed by agitating together definite amounts of salt and water give greater effects on the E.M.F.'s than was the case when the depolarizer was made by mechanically mixing the basic salt with the normal salt. It is quite logical to conclude that the basic salt coats or becomes an intimate constituent of the surface of the particles or crystals of the normal salt, when it was first realized³ that the basic mercurous sulphate was the main disturbing factor in the constancy of standard cells, it was thought that any commercial sample of mercuric sulphate might be satisfactory if treated with sulphuric acid so as to change the basic salt to normal and then properly preparing the paste so as to avoid forming the basic salt. A good grade of commercial mercurous sulphate was digested over night with a 12 times molecular sulphuric acid. The product was improved, but the cells in which it was used still clearly indicated the presence of basic salt. Whenever mercurous sulphate forms under conditions such that the basic mercurous sulphate may form, this basic salt appears to build into the crystal structure of the normal salt, so that treatment with sulphuric acid does not correct the difficulty. The basic salt does not appear where the sulphuric acid acidity is molecular or greater. This principle has permitted the preparation of normal mercuric sulphate both chemically and electrolytically.⁴

¹ Hulett: *Phys. Rev.*, **32**, 257 (1911).

² *Phys. Rev.*, **22**, 328 (1906).

³ *Trans. Am. Electrochem. Soc.*, **5**, 59 (1904).

⁴ Carhart and Hulett: *Trans. Am. Electrochem. Soc.*, **5**, 59 (1904).

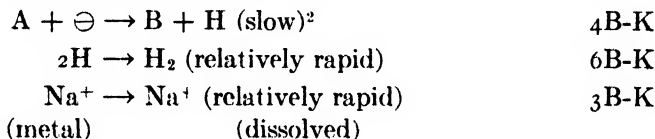
KINETICS OF THE DISSOLUTION OF DILUTE SODIUM AMALGAM*

BY ROBERT LIVINGSTON

Brönsted and Kane¹ have recently demonstrated that the rate of dissolution of sodium from a dilute amalgam into a solution of a weak acid is given by the following equation

$$-\frac{d(\Sigma\text{Na})}{dt} = k(\Sigma\text{Na})^{\frac{1}{2}}(\text{A}) \quad 1$$

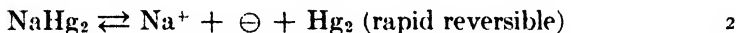
where (ΣNa) is the stoichiometric concentration of sodium in the amalgam and (A) is the concentration of the acid in the aqueous (or benzene) layer. In interpretation of these results, they advance the following mechanism.



While this mechanism affords an explanation of the proportionality of the rate to the concentration of the acid, it does not offer a direct explanation of the dependence of the rate upon the square root of the sodium concentration.

It is well known that sodium and mercury form the compound NaHg_2 . Evidence for the stability of this compound may be obtained (1) from the sharpness of the corresponding maximum in the melting-point curve,³ (2) from the high heat of solution of sodium in mercury,⁴ and (3) from the large difference of electrical potential between sodium and sodium amalgam.⁵

It seems probable therefore that the following equilibrium (which may take place in steps) is an important factor in determining the rate of dissolution.



The rate of reaction 4B-K is

$$V_{4\text{B-K}} = k_{4\text{B-K}} (\text{A}) (\ominus) \quad 3$$

But applying the mass action law to reaction 2

$$(\ominus) = K \left[\frac{(\text{NaHg}_2)}{(\text{Hg}_2)} \right]^{\frac{1}{2}} \quad 4$$

* Contribution from the School of Chemistry, University of Minnesota.

¹ Brönsted and Kane: *J. Am. Chem. Soc.*, **53**, 3624 (1931).

² A and B represent a conjugate acid and base respectively. See Brönsted: *Rec. Trav. chim.*, **42**, 718 (1923).

³ *Inter. Crit. Tables*, **2**, 436.

⁴ *Inter. Crit. Tables*, **5**, 202.

⁵ *Inter. Crit. Tables*, **6**, 332.

Since the greater part of the sodium exists as the compound, equation 4 may be written approximately as—

$$(\ominus) = K^1 (\Sigma \text{Na})^{\frac{1}{2}} \quad 4a$$

The combination of equations 3 and 4a leads directly to the empirical equation 1. It should be mentioned that no mechanism which postulates the existence of appreciable concentrations of the ion NaHg^+_2 need be considered, since such a compound, between the mercury molecule and the sodium ion (with its rare gas structure) would undoubtedly be relatively unstable.

In other amalgams where there is less tendency toward compound formation, the rapid reversible step may be



This reversible step would be consistent with an empirical equation similar to equation 1, if the metal were largely non-ionized; but if it existed chiefly as ions and electrons, the rate of dissolution would be directly proportional to the stoichiometric concentration of the metal. This suggests a possible explanation of the results of Fraenkel and Heinz⁶ on the rate of dissolution of alkaline earth amalgams.

Summary

A mechanism is presented for the dissolution of sodium from dilute amalgams.

⁶ Fraenkel and Heinz: *Z. anorg. Chem.*, **137**, 39 (1924).

While this paper was in proof two articles have appeared which discuss the results of Brönsted and Kane (1). C.V. King and M.M. Braverman (*J. Am. Chem. Soc.* **54**, 1744 (1932)) have studied the rate of dissolution of solid metals in acid solutions containing depolarizers, and have concluded that the rates are entirely determined by diffusion speed. L.P. Hammett and A.E. Lorch (*J. Am. Chem. Soc.* **54**, 2128 (1932)) advance the theory that the square root law is to be attributed to a phenomenon related to over voltage. Needless to say, the mechanism discussed here is a significant explanation only if the measured rates were not influenced by the speed of diffusion. (cf. Ref. 1, pp. 3634-5).

NEW BOOKS

A Text-Book of Experimental Cytology. By James Gray. 23 × 16 cm; pp. x + 516. New York: The Macmillan Company, 1931 Price: \$7.50. The chapters are entitled: the cell as a unit of life; the cell as a physical unit; cell dynamics; the cell as a colloidal system; the physical state of protoplasm; cell membranes and intercellular matrices; the nucleus; mitosis; cell division; the shape of cells; the growth of cells; cell variability; the equilibrium between a living cell and water; the permeability of the cell surface; the nature of the cell surface; contractile cells; phagocytosis.

"Until recently the central theme in zoological thought has been Evolution and whatever be the mechanism whereby one species has given rise to others we may be quite sure that the processes involved are essentially of a dynamic nature; the potentialities of the organism and the nature of the environment have operated together to produce new and varied forms of life. Any real insight into the causes of Evolution involves a knowledge of function, and any conception of the organism as a dynamic unit is incomplete without a knowledge of its evolutionary history. It is just as illogical to restrict the study of animal life to morphological observations as it is to study an aeroplane as though it were a static and inert machine. Precise knowledge of the reactions between an organism and its environment is, however, very rare in those cases where the sequence of evolutionary forms is best known, and students of Evolution must either be content with relatively vague and indefinite speculation or must set to work to analyse environmental responses for themselves," p. vii.

"Cytology may rightly claim to be the frontier state in the biological commonwealth, for within its borders biologists and chemists find common ground. The chemist is interested in the activities of living matter and the biologist is impressed by the orderly analysis to which the chemist can submit his facts. A biologist who attempts to give a generalised conception of the living cell inevitably invites active criticism, for the attempt to co-ordinate the relevant facts is fast becoming a task beyond the competence of any one individual. Sir William Hardy has recently described the ideal biological college: 'It should have three floors—a ground floor for molecular physics, a first floor for biophysics, and a top floor for cell mechanics.' The present book represents an honest, if pathetic, attempt to creep downstairs. It represents the impressions which the author, as a biologist, has gained by contact with such physical facts as appear to him to bear on the structure of living matter, and which can be imparted to others like himself, whose knowledge of inanimate matter is limited," p. viii.

"As a physiological unit the rôle of the individual cell is not quite so clear. In the first place the cell is not a fundamental unit in the sense that any process of subdivision leads to a complete disorganisation of its properties. An enucleated fragment of an amoeba or of a sea urchin's egg is by no means dead, but retains for a considerable time typical properties of living matter; bacteria are alive, yet their structure is by no means similar to that of a typical cell; fungi are also alive, and yet they exhibit no cell structure in the strict sense of the word. Difficulties of this kind have perplexed cytologists for many years and are still real objections to the time-honoured Cell Theory," p. i.

"Even within inanimate colloidal systems the statistical laws break down when we deal with units which are no larger than typical living cells. Using a suspension of gold particles, whose average radius was $19\ \mu\mu$, Smoluchowski (see Svedberg, 1928) found that within a volume of the suspension equal to $1064\ \mu^3$ (i.e. the approximate volume of many living cells) there was an average number of particles equal to 1.545. When this small volume of suspension was examined from time to time, however, the actual number of particles visible varied very considerably—sometimes no particles were visible, at other times as many as seven could be seen. This variation is, of course, due to random Brownian movement," p. 7.

"Quite clearly the degree of statistical variation which will occur in molecular systems depends largely on the magnitude of the system examined. If we examined 1 cc. of the gold

suspension the amount of variation would be relatively small: if we use a volume of $10 \mu^3$ it will be very large indeed. As long as we are dealing with large systems, any significant variation in the distribution of matter or energy occurs for such short periods of time or on so very few occasions, that we are justified in ignoring any state other than the one which is the most probable. In other words, in large systems the statistical possibilities postulated by the kinetic theory of matter are arbitrarily eliminated by assuming the truth of the Second Law of Thermodynamics," p.8.

"A more adequate picture of intracellular oxidase systems is available from the work of Keilin (1925, 1926, 1929). Keilin showed that nearly all cells contain an oxidisable pigment, *cytochrome*, which, in the reduced form, exhibits a definite series of spectral bands. If a suspension of cells in an oxygenated medium is examined spectroscopically no spectral bands of cytochrome are visible; if, however, the oxygen be removed, four distinct bands of reduced cytochrome become visible, which again disappear on admitting oxygen. We may conclude, therefore, that oxidised cytochrome is rapidly reduced by the cell and that reduced cytochrome is rapidly oxidised by atmospheric oxygen. In other words cytochrome can act as carrier of oxygen.

"Keilin has shown that cell narcotics, e.g. urethane, can prevent the reduction of cytochrome but they do not inhibit its oxidation. For instance, if ethyl urethane is added to a yeast suspension, the cytochrome is immediately oxidised and is not reduced on the removal of oxygen. On the other hand, a trace of cyanide will immediately reduce oxidised cytochrome, and will prevent its oxidation by free oxygen. There are, therefore, two distinct processes at work—those concerned with the oxidation of reduced cytochrome and those concerned with the reduction of oxidised cytochrome; the cytochrome is acting normally as an intermediate carrier of oxygen between these two processes. Keilin (1929) has recently shown that the systems responsible for the reduction of oxidised cytochrome are the dehydrogenase system of enzymes, whereas the catalyst responsible for the oxidation of reduced cytochrome is none other than the indophenol oxidase system so universal in animal tissues. All factors which influence the activity of dehydrogenase enzymes inhibit the reduction of cytochrome and all factors inhibiting indophenol oxidase inhibit the oxidation of cytochrome. It looks as though the 'respiratory ferment' of Warburg is really the indophenol oxidase system, and that it is only a part of the whole respiratory mechanism," p. 20.

"The conception of the cell as a colloidal system is probably one of the most important landmarks in the history of cytology. For nearly a century our knowledge of cell structure was based, not on observations of living units but upon cells which had been stabilised by fixation and artificially differentiated by staining reactions. Almost simultaneously, Fischer (1899) and Hardy (1899) demonstrated, without any element of doubt, that these standardised but arbitrary processes were of the same fundamental nature as those which effect the precipitation of inanimate protein systems and which control the uptake of dyes by the coagulated particles. This fundamental discovery showed that the only reliable guide to protoplasmic structure must lie in a study of uncoagulated colloidal systems and not in a meticulous observation of coagulated cells. For more than thirty years every student of cell structure has had, of necessity, to follow the rapid march of colloidal chemistry. To some extent the position is satisfactory: the colloidal properties of cell constituents are now realised and we are not likely to make very gross errors in the interpretation of cell structure. At the same time, we must constantly bear in mind that the living system is incomparably more complex than any which has, so far, attracted the undivided attention of the chemist," p.33.

A priori, one would suspect the phenomena of *antagonistic ion action* to be concerned with the equilibrium between metallic ions and protein systems, and to a significant extent this view is supported by experimental facts. There always remains, however, one outstanding difficulty. From a chemical point of view the equilibrium between proteins and potassium ions is very similar to the equilibrium between proteins and sodium ions, and yet the biological properties of the two ions are profoundly different," p. 47.

"Except in the particular case of the Feulgen reaction it is not very easy to assess the cytological value of microchemistry. When we state that protoplasm invariably contains

proteins and derivatives of the fats, the contribution to cytology is comparable, in aeronautics, to a statement that an aeroplane invariably contains iron and copper. Either the essential constituents of the living machine are composed of protein and lipoids or they are orientated in a matrix of these compounds. Both for a study of the cell and of an aeroplane we require to know not only the shape and function of the various chemical constituents, but we want to know how they are oriented in respect to one another to form a working and useful unit," p. 84.

"It has been long known that the hyaline surface of a cell is instable in the absence of divalent cations (e.g. calcium, magnesium) from the external medium. In the absence of calcium no hyaline surface forms on an echinoderm egg, and in 1900 Herbst showed that in calcium-free sea-water the intercellular matrix of an echinoderm larva is dissolved and the cells separate freely from each other. In the case of *Mytilus* tissues the matrix is disorganised if magnesium is absent (Gray, 1926), whilst Galtsoff (1925) found that calcium and magnesium are both required for the reunion of artificially separated sponge cells. We thus reach the conclusion that the normal elastic surface of the cell is a gel whose cohesive properties depend upon the presence of divalent metallic ions. The only compounds which appear to have the property of forming cohesive membranes in the presence of calcium appear to be the proteins and possibly some of the polysaccharides. If substances such as gluten, casein, or mucin are powdered and rubbed with a little water they readily yield a tough coherent mass which is practically insoluble in water, and which can be pressed out into a more or less transparent membrane. The factors influencing the stability of such protein gels are strikingly similar to those which influence the stability of the hyaline gel which binds together the cells on the gills of *Mytilus edulis*," p. 107.

"The universal presence of nucleic acid in animal nuclei leaves little doubt that this compound is essentially the same as the 'chromatin' of histologists. Free nucleic acid has just those affinities for basic stains as are characteristic of chromatin, and the variation in the staining properties of the kinetic nucleus are paralleled by the staining properties of nucleic acid when saturated to varying degrees by combination with basic proteins. The evidence supporting an identity of chromatin and nucleic acid is greatly strengthened by the recent work of Feulgen and others. If a tissue be exposed for a suitable time and at a suitable temperature to a solution of mineral acids the distribution of chromatin can be detected by subsequent staining with acid fuchsin," p. 128.

"The most direct proof that the asters form an active part of the cleavage mechanism is provided by the fact that any irregularity in the size or position of these structures is invariably accompanied by an irregularity in the form and position of the cleavage furrow," p. 201.

"In 1919 Hartridge suggested that the characteristic discoidal form of mammalian erythrocytes is an adaptation to the physiological functions of the cell. In order that oxygen should reach the centre simultaneously from all points of the surface, the cell must be either a sphere or an infinitely thin disc. If the red blood cell were spherical, however, it would present a minimum surface per unit volume, and consequently the rate at which oxygen would enter would be reduced to a minimum. In a flat disc, however, oxygen would reach the centre more readily at the periphery than elsewhere. The peculiar form of the mammalian erythrocyte compensates for this by its greater thickness at the periphery—so that oxygen will reach the centre of the cell simultaneously from all part of its surface," p. 263.

H. V. Wilson found that "if the tissues of the sponge *Microciona* are cut up into small fragments and squeezed through bolting silk, the resultant pulp of cells is capable of re-organising itself into compact tissues or even into new sponge individuals," p. 297.

"There is so much evidence to show that the cell surface is not equally freely permeable to both anions and cations, that one tends to overlook the fact that nevertheless a growing cell must be in a position to absorb both types. How far the recent work of Mond (1927) throws light on this difficulty remains to be seen. Mond has shown that if red blood-corpuscles are on the acid side of their iso-electric point their chlorine content goes up and their potassium content goes down, whilst on the alkaline side the relative concentrations are reversed," p. 370.

"Ruhland (1908-13) showed that there are a number of dyes (e.g. methylene green and thionin) which enter cells readily but which will not dissolve in cholesterol: similarly there are a number of 'fat-soluble' dyes (cyanosin, Bengal rose) which will not enter the living cell," p. 371.

"He points out that the ability of dyes to enter a plant cell is often less than its ability to enter an animal cell, and that this is particularly obvious when the fat-soluble dye is in the colloidal state: it is therefore possible that the failure to enter the plant cell may be due to the inability of a molecular aggregate to penetrate the cellulose wall. If this conclusion is justified, one grave objection to Overton's hypothesis disappears, but it is still necessary to account for the fact that methylene green and thionin (both insoluble in lipoids) will enter both animal and plant cells. Hertz (1922) showed that the entrance of these dyes into *Opalina* is unaffected by the presence of anaesthetics, whereas the entrance of fat-soluble dyes was inhibited. Höber, therefore, suggests that lipid-soluble and non-lipid-soluble dyes enter by a different mechanism. Similarly Nierenstein (1920) found that an adequate correlation between the ability of basic and acid dyes to enter *Paramecium* and their partition coefficients between a fat-soluble substance and water only exists when the fat solvent (e.g. olive oil) contains both a base and an acid (e.g. diamylamine and oleic acid). So far as these facts can be summarised, they seem to suggest that most cell surfaces are permeable to those dyes which can either (i) dissolve in fats, or (ii) react with some constituent of the membrane, provided that in all cases the molecular aggregates of the dyes are not beyond a certain maximum size (Höber and Kempner, 1908; Höber and Chassin, 1908)," p. 372.

"The relationship which exists between a contracting muscle and diffusible ions has also been investigated by Mitchell and Wilson (1921), who found that when frog's muscles are stimulated to contract under conditions which do not involve irreversible stages of fatigue, the cells lose no more potassium than is attributable to a potassium-free medium; on the other hand, it is only during contraction that a muscle will absorb rubidium or caesium. The interpretation of these facts is not easy, but they indicate that the act of contraction alters in some way the diffusibility of electrolytic ions. Parallel to McClendon's results with excited muscle fibres are the observations of Blackman and Paine (1928) on the exosmosis from the pulvinus of *Mimosa* during stimulation," p. 401.

Wilder D. Bancroft.

The Adsorption of Gases by Solids. *A General Discussion held by the Faraday Society, Jan. 1932. 25 x 16 cm.; pp. iii + 318, London, Gurney and Jackson, 1932, Price: 15 shillings.* It is important now and again, for scientists in any particular field to get together and thrash out the various problems, experimental and theoretical, which may have arisen during a period of years. The frequent discussions organised by the Faraday Society bring together workers in many branches of physical chemistry and perform a valuable service. All such discussions tend to centre on the more recent developments and the volume under review is no exception. In the nature of things, however, the substance of a number of the papers is to be found in many journals and proceedings published during the last few years.

The papers are collected under three main heads; Experimental Methods, Kinetics and Energetics of Adsorption, and, finally, Theories of Adsorption. The adsorptive properties of glass vessels are well known and the necessity of using clean de-sorbed glass has made most chemists and physicists familiar with the elementary principles of adsorption. The growth of experimental evidence during recent years has led to the recognition of more than one type of adsorption.

At very low temperatures gases are strongly adsorbed by solids. At moderately low temperatures the adsorption passes through a minimum and at high temperatures strong adsorption sets in again, followed by a decrease at still higher temperatures. Adsorption at low temperatures is associated with small binding energy and is generally ascribed to forces of the van der Waals type. The term "dispersion forces" is also used by some continental writers to describe the same phenomena. The heats of adsorption at these low temperatures are generally of the order of one or two thousand calories per gm. molecule of gas adsorbed. Adsorption at liquid air temperature is usually instantaneous, but high temperature ad-

sorption proceeds with a measurable velocity, which increases rapidly with temperature, and because of this analogy with chemical reactions has been termed "activated" adsorption by some writers, "chemisorption" by others. An activation energy is required for this type of adsorption and evidence is brought forward in the introductory paper to show that this energy is acquired after contact with the solid has been attained. If the necessary energy were possessed by the impinging gas molecules, the quantity of gas adsorbed in a given time should be much greater than is actually observed. The heats of adsorption associated with the high temperature phenomena are roughly ten times those associated with the van der Waals or low temperature adsorption. Further distinctions between the two types of adsorption can be made. In low temperature adsorption the sorbate is recoverable by pumping. With "activated" or "chemisorption" the gas is sometimes recoverable, but frequently the process is irreversible. The well known case of oxygen and charcoal is an example of the latter type, where the oxygen is usually given off as oxides of carbon. Apparently the C-O binding is stronger than the C-C binding of the solid at high temperatures.

Of special interest in the first section one may note the discussion on the determination of the specific surface in the introductory paper, the use of thermionics in adsorption problems, and the question of the mobility of adsorbed atoms which is discussed, *inter alia*, by many of the contributors. One may venture the opinion that the work of Langmuir, Becker and others on the effect of adsorbed layers on the thermionic properties of metal wires, and the work of Volmer and his school on the mobility of adsorbed molecules are the most elegant experimental methods of recent years, which are likely to have a fundamental bearing on the theoretical development of the subject. The unique properties of electron beams in discovering the arrangement of adsorbed gas molecules are likely to be much used in the near future, although the applications may be somewhat limited. The method may be restricted to low-velocity electrons in high vacua. It is possible that a study of the melting properties of two-dimensional adsorbed films may be of the utmost importance in the theory of the liquid state. Another paper in this section deals with the sorption of gases by glass, and although the pressures are too high to be of practical interest to those who use high vacua, one notes with interest the effect of various treatments, such as washing and annealing the glass surface. This raises the vexed question of the preparation of adsorbents which is also discussed by other contributors.

The second part of the discussions on the kinetics and energetics of adsorption processes contains many interesting papers. The use of the *ortho-para* hydrogen conversion in adsorption problems is specifically discussed in several papers and appears to have aroused a good deal of interest. The mechanism of the catalysis of ammonia on tungsten is also very thoroughly dealt with, and the occlusion of hydrogen by palladium is considered in a series of papers from Oxford. Interest in this section will perhaps, however, centre on the discussion of discontinuities in adsorption processes, to which several groups of workers have now testified. It appears that the adsorption isotherm is not really a continuous curve but a succession of sharply defined loops concave to the pressure axis. Discontinuities have been observed with charcoal, silica gel and copper and iron catalysts as adsorbents. It is too early to give adequate reasons for the discontinuities and the general impression derived from these discussions is that much more data are required before a solution of the problem can be reached.

One of the outstanding difficulties of all work on adsorption is connected with the adequate preparation of the adsorbent for the experiments. It is an unfortunate fact that most of the substances suitable from the point of view of porosity and large specific surface area are almost completely unknown from the structural point of view. In order to free any surface of gas it has been necessary, until recently, to degas the material to a comparatively high temperature, and this procedure has automatically produced sintering of the adsorbent and alteration of surface area, etc. Considerable doubt may, in fact, be expressed as to whether adsorbents treated in this manner are gas-free. Consequently, one is led to the conclusion that many of the values for λ , the heat of adsorption, whilst no doubt reliable for the particular complex examined, should be taken as the heat of adsorption of gas A on the gas-solid complex B-C rather than the true value of λ for the complex A-C. The discussions under

review emphasized, to one reader at least, the importance of a new method of producing a clean adsorbent. This method consists essentially in passing a stream of vapour, such as CCl_4 or CS_2 , over the adsorbent. It is even suggested that a connection exists between "activated" adsorption and gas displacement effects. The process which requires energy of activation may be that of displacement of residual gas from the adsorbent by the adsorbed gas.

The final section contains many papers of great interest. Before passing on to these, one may note an interesting paper on accommodation coefficients where the interchange of energy between gas atoms and solid surfaces is shown to depend on the cleanliness of the adsorbed surface. As an example one may compare the older value of 0.3 for helium and tungsten with the recent value of 0.057. The introductory paper to section 3 consists in a general theoretical survey in which the influence of electrostatic forces, valence forces (of the Heitler-London type) and van der Waals forces on adsorption are considered. The paper on accommodation coefficients already referred to presages the fact that the interactions of gas and solid can only be fully worked out by the applications of the methods of wave mechanics. At the risk, therefore, of presenting the gist of this part of the discussion in an unbalanced manner, one would like to attempt a summary of the theory of Lennard-Jones which has already explained a number of adsorption phenomena in more than a qualitative manner.

The low temperature, or van der Waals type of adsorption is first discussed. All of the ultimate reactions between atoms and molecules, whether they be in the same phase or not, must be explicable in terms of the interactions of the systems of electrical charges of which they are constituted. It is now known that atoms attract each other at large distances according to an inverse seventh power law and this "seems to be due to a sympathetic fluctuation of the electron space clouds of the two atoms which produces in the atoms effective dipoles tending to move more in phase than out of phase." The case of the interaction of gas atoms and a metallic conductor is considered, modern theories allowing the latter to be regarded as a perfectly polarizable system. The interaction of the gas atom and the metal can then be treated according to the classical method of electrical images and the potential energy of the atom due to its image is given by $mc^2\chi R^{-3}$ where m is the mass of the electron, c the velocity of light, χ the magnetic susceptibility of the gas atom, and R its distance from the metal surface. From this it has been possible to estimate the heats of adsorption of argon, hydrogen and nitrogen on copper. The figures obtained are of the same order as the observed values. The potential fields of argon and neon outside crystals of KCl and NaF are considered, and it is pointed out that these fluctuate according as the gas atom is above the centre or corner of a unit cell. The surface of a crystal from the point of view of a gas atom outside it is a regular series of mountains and valleys. The theory is then developed qualitatively to include the phenomenon of "activated" adsorption to include the phenomenon of "activated" adsorption of, for example, hydrogen on a metal. The cohesion between the metal and a hydrogen atom is supposed to be greater than half the dissociation energy of H_2 and the height of the point of intersection of the potential energy curves of the two systems metal and molecule, and metal and atom $A + \text{atom } B$ gives the activation energy for a transition from metal + molecule to metal + atoms. The conceptions of the metallic state which have had so much success in explaining the phenomena of thermionics and electrolysis are seen to throw considerable light on the current problems of adsorption. The theory is further applied to the slow sorption of hydrogen on copper to which experimental observations had also attributed an energy of activation and a simple interpretation of this quantity is given. It may be added that the conception of two-dimensional melting involves the penetration of the potential barriers of the crystal surface already referred to. The mathematical difficulties confronting the worker in this field, are, to say the least, very considerable, and one feels that the way to a better understanding of the fundamental processes of adsorption phenomena has been pointed out. The volume should be of considerable value and inspiration to all workers on the subject. The introductory papers alone form an admirable synopsis of the present stages of development and are worth study by those to whom the subject is only of general and not particular interest.

J. T. Randall

Repertorium der physikalischen Chemie. By H. Zeise. 21 × 13 cm; pp. vi + 215. Leipzig and Berlin: B. G. Teubner, 1931. Price 8 marks. Dr. Zeise has skilfully compressed into about 200 pages of well printed and illustrated text a surprising amount of clear and accurate information. The size of the strongly bound book enables it to be carried in the pocket and makes it suitable for reading at odd moments as well as for sustained study. All the important branches of the subject are covered and the treatment, whilst thoroughly modern, is not out of balance. The sections on quantum mechanics, wave mechanics, spectra (including band and Raman spectra), atomic and molecular structure, types of linking and strong electrolytes are clear and intelligible and really convey information, yet the sections on the properties of gases, solutions, thermodynamics, phase rule and electrochemistry are equally good and as carefully developed. The book is one which can be warmly recommended and its low price is a welcome feature in these days of expensive books. The student who reads German will find it most useful in revising a large amount of material, and the chemist who is not a specialist in physical chemistry will get from its pages a good understanding of modern developments in that science. There are several misprints and quite minor errors besides those listed on p. vi; for example in the discussion of isotopes on p.5, and in the values of the potential of the decinormal calomel electrode on p.201, which have not been corrected for the arithmetical error in Randall and Young's paper. It is unusual to apply Pauli's principle to five quantum numbers (p. 24). A reference to Sutherland's formulae might have been given on p.107 (it is given on p.111), and something said about recent investigations as to its validity. The statement on p.123 that the different specific heat curves of the solid elements in Fig. 36 are due to different expansions does not seem correct, since the abscissae are not reduced temperatures. J. R. Partington

Gmelins Handbuch der anorganischen Chemie. Edited by R. J. Meyer. Eighth edition. System-Number 7. Brom. 25 × 16 cm; pp. xxxvi + 342. Berlin. Verlag Chemie, 1931. Price: 56 marks (Subscription price 49 marks). With the publication of this section the great treatise on inorganic chemistry moves a step further towards the goal of completeness which, in some past works of this type, has proved a limit reached asymptotically. The rate of progress seems to promise that the whole work will be achieved within a reasonable time, and that the earlier sections will not be completely out of date by the time the later ones are issued. The present volume on bromine sustains the excellent standard of previous ones, the element and its compounds with water, hydrogen, oxygen (including oxyacids), nitrogen, fluorine and chlorine, being considered from all points of view, physical, physico-chemical and purely chemical, with great completeness. The information is up to date: there is a long section, for example, on bromine oxide, and the optical proof of the existence of bromine chloride is also described in detail. A great amount of numerical information is incorporated into the text, and there are useful curves and figures. The information on technical processes is quite detailed, and includes the aniline precipitation method tried out by the Ethyl Gasoline Corporation. The section on technical purification of bromine is fuller than usual, and there is a long section on production data. In view of the strong contradictory experimental evidence, the long section on the Budde effect and the effect of moisture on it, might have been shortened with advantage. J. R. Partington

Physikalisches Handwörterbuch. Edited by A. Berliner and K. Scheel. Second edition. 28 × 20 cm; pp. vi + 1428. Berlin: Julius Springer, 1932. Price. 96 marks, bound in cloth 99.60 marks. The book under review is the second edition of a work which, inscribed to Nernst on the occasion of his sixtieth birthday, first appeared in 1924. The new version has been brought up to date in a comprehensive manner, which has involved increasing the number of pages by well over one-half. But, printed as it is, on thin but good paper, in adequate type and with two columns per page, it remains a volume of reasonable size, convenient to handle and to read.

For the contents, there can be little but praise. Designed by the editors, not so much for the physicist who wishes to obtain a first broad impression of subjects outside his own special field, as for those who use the science of Physics "als Hilfsfach," it appears to the

reviewer that it is a volume which will be of emphatic service to any physical chemist who has access to it. For, whilst there are paragraphs or articles on all the usual topics hitherto comprised under physical chemistry in its narrower sense, these are generally very brief, much more attention being paid to aspects of theory and of technique, with which most of us have had a rather perfunctory acquaintance in the past, but with which it is increasingly important that we be familiar. And, as far as the reviewer can judge, the contributions maintain throughout a high level in respect of accuracy, conciseness and clarity.

At the risk of appearing invidious, a few of the topics treated will be selected for specific mention. The *Atom* and the *Atomic Properties* are dealt with in a series of articles covering ten pages, written by Hahn, Gerlach, Kohlrausch, Scheel and others. Here, as elsewhere, a number of contributions are unsigned. The whole forms a compact and authoritative summary. *Explosions* are treated in seven pages, chiefly by Wendlandt, and the very informative article on *Glass* (by R. Schaller, of Jena), is of the same length. Eight pages are devoted to *Colour* and to related subjects which, between them, cover a very wide field. *Photometry* is dealt with from many points of view by Liebhent (17 pp.). Eleven pages cover various aspects of the older and newer *quantum theory*. The articles are unsigned. The subject of *crystals* is treated in considerable detail by Schiebold (32 pp.). *Heat* and related subjects occupy 14 pp., written by such authorities as Henning, Scheel and Gröber. Henning is responsible for most of the articles on *thermodynamics*, good representative contributions being those on *Entropy*, *Gas Degeneration*, and *Equations of State*. W. Jaeger writes, inter alia, on *Galvanometers*, and deals authoritatively with *electrical units* and their dimensions. The articles on *Dark-Field Illumination* and *Ultramicroscopy* by M. Berck and on *Diffraction* by Boegehold, on *Hardness* (Schleicher) and on *Plasticity* (Nádai), are typical of the useful and competent material with which the book is packed. *Radioactivity* is accorded full treatment—thus the contribution by Kohlrausch on *Actinium* occupies three pages.

Good typical articles on physico-chemical themes are those by Wohl on *Reaction Velocity* and on *Gas Equilibria*, but frequently, though chemists need not complain, the treatment of such subjects is so very brief as to make it doubtful whether it retains any value. Schwab writes in an interesting way on *Activation*. A note of a different kind is struck in the contributions by Reichenbach entitled *Wahrscheinlichkeit* and *Wahrheit*.

Beyond the matter just touched on, it is difficult to criticise. The short article on *Drying* is without value; reference is made to a laboratory manual of organic chemistry as the authority on the subject. The relative lengths of the contributions vary somewhat curiously in certain cases. Three pages on *Isomerism* hardly compensate for the fact that only about half this length, in all, is devoted to the subjects of *Alloys*, *Solubility* and *Solution*. But emphasis on such minor points would be ungracious; the editors, in face of the familiar difficulties which they describe in their preface, have achieved a very considerable success, and one which will be really appreciated by all who use the book. A. J. Allmand

Rechenverfahren und Rechenhilfsmittel mit Anwendungen auf die analytische Chemie.
By Otto Liesche (*Die chemische Analyse. Band XXX.*) 25 × 16 cm; pp. viii + 201.
Stuttgart: Ferdinand Enke, 1932. Price: 20 marks, bound 22 marks. In this monograph Professor Liesche deals entirely with arithmetical processes as applied to chemical science. The object is to instruct the student how to shorten his computations and to make him familiar with the theory underlying each method. The author holds that axiomatic truths are neglected or are not properly mastered either at school or university. Hence the detailed explanatory statement accompanying each method he describes, which should prove most useful not only to teachers in secondary schools and institutes but also to workers in chemical laboratories. The author revises Seneca's view of school and after life and writes "Non vitae sed scholae discimus" and we agree with him when the phrase is applied to mathematics, the basis of all physical science. Many school problems are rather artificially set, as the boy finds when he becomes a laboratory worker. Thinking on inductive lines should be more prevalent than it is in schools. The processes of deduction are more appropriate in later life. Every schoolboy with average brains should leave school well grounded by practice in

arithmetical processes. The author strongly recommends the methods of exposition devised by Dr. Ferrol and holds that formidable looking problems yield simple and spontaneous solutions if Ferrol's technique is used. We agree that a careful study of Ferrol's processes would be a great advantage to the scholar. He would be trained in algebraic thinking of a character most useful in after life in the laboratory. We fear however it will take some time for Ferrol's method to penetrate in schools.

The first chapter of Dr. Liesche's book is devoted to an exposition of the four rules of arithmetic, using Ferrol's processes. Logarithms, the slide rule and calculating machines are discussed in a wholly elementary manner in the second chapter. We think the slide rule should give place to the calculating machine in all laboratory calculations where multiplication and division are necessary. Time is lost in logarithmic computations and there is a loss of accuracy in using the slide rule. In describing the Brunsviga the author mentions Leibnitz as the first inventor of a calculating machine but omits to notice the pioneer work of Babbage in this country. The calculating machine is merely a time-saving device but this is what is wanted in a laboratory. The worker is saved mere mechanical mental activity and is free to apply his mind fully to the theoretical side of his problem.

The author shows in the third chapter how algebra can be used effectively in computations as a time-saving device, particularly in problems of physical chemistry such as mass action problems. The fourth chapter is devoted to an elementary exposition of nomography, the name given by d'Ocagne in 1884 to describe the graphical method of solving all equations of a given type by means of one diagram. A simple example is a quadratic equation of the type $x^2 + ax + b = 0$. A diagram constructed to solve an equation of this type is called a nomogram. A number x is determined by means of a nomogram when two numbers a and b are given. Two straight lines for a and b are graduated and the x curve is so graduated that if a straight line is drawn joining the graduation a on the a scale to the graduation b on the b scale the line cuts the x curve at the graduation x where x is the desired result. Nomography is a new branch of applied geometry and a nomogram if the scales are fine enough dispenses with the solution of the equation. In general the worker gets at once a result approximately correct. Nomograms can be prepared for simple addition, subtraction, multiplication and division, for logarithmic and trigometrical functions and also for empirical data. The reader is shown how to prepare nomograms applicable to chemical problems.

The list of nomographic literature given is incomplete. All the German publications are mentioned but the author appears to be unaware of Brodetsky's "First Course in Nomography" published in 1925 by Messrs. G. Bell & Sons. We recommend Dr. Liesche's monograph to teachers of elementary chemistry and to all laboratory workers.

J. F. Tocher

Photochemical Processes. *A General Discussion held by the Faraday Society, April 1931. 25 × 15 cm.; pp. 218. Aberdeen: The University Press, 1931. Price: 10 shillings, 6 pence.* This volume is an account of the fifty-fifth general discussion organised by the Faraday Society, and is mainly a review of the progress made in photochemistry since the last discussion in the subject which took place at Oxford in 1925 (Photochemical Reactions in Liquids and Solids, *Trans. Faraday Soc.*, 21, 437 (1925)). The meeting was held at the University of Liverpool under the chairmanship of the President (Dr. Robert L. Mond). It was attended by eleven overseas guests who as authorities in the subject brought important contributions. There were in all four sessions. The first of these comprised a discussion and contributions of new researches on molecular spectra in relation to photochemical change. The introductory paper by Professor R. Mecke included an interesting historical account of this comparatively recent branch of photochemistry, which has helped so much to elucidate the early stages of photochemical changes. The second and third sessions were devoted to the consideration of photochemical changes in (1) gaseous, and (2) liquid and solid, systems. The sessions were opened by suggestive addresses delivered respectively by Professors Max Bodenstein and A. Berthoud and were followed by a considerable number of contributions on special aspects of the subject. The fourth session on photosynthesis was introduced by Professor E. C. C. Baly and was also followed by an illuminating general discussion.

A comparison of the volume with that issued after the meeting at Oxford in 1925 shows that considerable success in the meantime has been attained in interpreting the results obtained with the spectroscope, whereas the theories advanced to account for most of the complete photochemical changes are still uncertain. Nevertheless it is an uncertainty which has provided entrancing problems for solution. The survey of the position of the subject presented is so comprehensive, and the references given so complete that the volume will be an invaluable aid to students and a necessary reference book for research workers in the subject.

D. L. Chapman

Atomtheorie und Naturbeschreibung. By Niels Bohr. 24 × 16 cm; pp. iv + 77. Berlin: Julius Springer, 1931. Price: 5.60 marks. This book consists essentially of four articles previously published separately in *Die Naturwissenschaften* and originating mainly from addresses delivered by Professor Bohr to various Scientific Meetings and Congresses. They are preceded by a valuable Introductory Survey (written in 1929, with an addendum dated 1931), which serves as a useful guide to the origin, nature, and development of the facts and theories discussed in the four sections of the book.

Many thousands of readers in all parts of the world will welcome the appearance of this volume. Practically without the use of mathematical symbolism, the whole history of the origin and development of modern atomic and quantum theory is given to the reader by the man who has played the leading rôle in this immense advance of science. It would be a great mistake to imagine that we have here simply a historical account, however, admirable and lucid, of the subject. What is most significant and most important to the reader is the profoundly philosophical and—let it be added—profoundly sane character of all Bohr's thought and reasoning. This is particularly true of the great events of 1925 and afterwards. Every physicist knows the fundamental part that the great pioneer of 1913 has played in the most recent advances of quantum mechanics. What Heisenberg has most aptly named the *Kopenhagener Geist der Quantentheorie* is evident in every page of this book. Bohr is not only a great and original discoverer in theoretical physics, but also and *always* the profound philosophical thinker, who, rising above symbolism, perceives the inner meaning of the facts and the conceptual relationships employed in the interpretation and representation of these facts. Nothing could be finer than the exposition given here by Bohr of the limitation placed by the observer (or observing instrument) on the reality of the thing observed, and the consequent *complementarity* (to use Bohr's own expression) of the space-time description on the one hand and the principle of causality on the other. As the reader progresses in the careful study of this book he finds, even though he be not a theoretical physicist, that he is gradually acquiring a very precious possession, namely a real insight into the revolutionary change of thought which modern quantum mechanics has brought about. Great indeed as was the change of thought caused by the work of Einstein and Minkowski and those who have followed them, it is probably no overstatement to say that quantum mechanics has led to an even greater change in the scientific outlook, and that Bohr has been the leader in this tremendous *mutation* of thought, which has brought a disciplined and restrictive sanity into the effort of the human mind to find an adequate *Naturbeschreibung*.

In the latter part of the book (addresses of date 1929), Bohr introduces ideas which may be destined to exert a great influence on the development of biological and psychological science. He raises the question, for example, whether the peculiar characteristic of the phenomena of the living organism may perhaps reside in the impossibility of a deep analysis of the physical conditions of such phenomena. An atomic analysis of a living organism would, in fact, require for its adequate specification a manifold of measurements and observations which would be incompatible with the stable existence of the organism. It must be confessed that this statement may be a very inadequate, or indeed possibly an erroneous, expression of Bohr's train of thought. He is such a profound thinker that it is not easy to follow him into an entirely new field of ideas. But one gains the impression that he regards a living organism as a system which may not be susceptible to experimental definition in terms of the measurements and concepts which are applicable to inanimate physical systems. It is to be hoped that Bohr will develop this train of ideas. Quantum mechanics can deal

statistically with an inanimate system of atoms. A living cell or a living organism is an organised market of exchange (of energy and atoms) with its external environment. The world of science has long been waiting for some new fructifying and *precise* concept, or a series of concepts, which will make a fundamental advance in the understanding and investigation of the phenomena presented by the process of life. So far, thermodynamics alone has given help. Is there some unitary or indivisible x which, incorporated into a higher thermodynamics (in the sense that quantum mechanics is a higher mechanics) will yield the desired result?

F. G. Donnan

L'Atome de Bohr. By Léon Brillouin. 24 × 16 cm.; pp. 363. Paris Les Presses Universitaires de France, 1931. Price: 100 Francs. The subject matter of this volume was first presented in a course of lectures given in 1928 at the University of Wisconsin, and later at Sorbonne. It concerns the older now classical view of the theory of spectra which owed its being to the speculations of Bohr.

The author devotes the first third of the book to an examination of the laws of physics of twenty years ago which were capable of being represented by a set of logically inter-related differential equations. It is shown how these equations cease to be valid when applied to the interior of the atom.

The theories of quanta, the Stark effect, the Zeeman effect, optical spectra, structure of multiplets, the spinning electron, X-ray spectra, and the laws governing the intensity of spectral rays are dealt with in separate chapters in such a manner as to prepare the reader for the next step in the line of historical development, that is, the more recent advances of wave mechanics.

This is a very clear exposition of the Bohr atom, and will prove to be of great value to students of molecular physics for many years yet.

W. E. Garner

Recent Advances in Organic Chemistry. By A. W. Stewart. Sixth edition. 22 × 15 cm; Vol. I, pp. xii + 429, Vol. II, xi + 432. London: Longmans, Green & Co., 1931. Price: 2 shillings each volume. This Edition of an already well known book contains new chapters on the Polymethylenes, Isomerism in cyclic compounds of the Decalin type, the Diphenyl problem and Di- and Tri-terpenes. A survey of the general methods for the preparation of polymethylenes and an account of the synthetical methods of Ruzicka for the production of large carbon rings are given. The constitution of Civetone and the nature of Muscone are discussed. Baeyer's Strain theory is outlined and the theory of strainless rings indicated; this subject is further developed in the later chapter dealing with the isomerism of the decalin type. The diphenyl problem is treated chronologically and the work which culminated in the collapse of the Kauffert hypothesis is described. The significance of the resolution of 3:3'-diaminodimesityl and of a *peri*-naphthalene derivative by Mills is pointed out. An extension of this chapter to include other examples of molecular dissymmetry such as the spiran type would be of value. The methods employed in the study of Di- and Tri-terpenes are outlined by reference to work on the Camphorenes and Squalenes.

A considerable extension of existing chapters has been made. The skeletal relationships of the terpenes are now emphasised with advantage. The synthesis of Norpinic acid and industrial methods for the production of camphor are new features. A brief account of Eudesmol is also included. Reference to the formation of "sugar carbonates" and "acetone compounds" and a fuller account of the oxidation of methylated sugars are welcome additions to the chapter on the carbohydrates. The use of O-monobenzoylphloroglucinaldehyde in the synthesis of anthocyanidins is a valuable extension of the chapter on this group. Other new features are an outline of Staudinger's views on the structure of ozonides and the introduction of a short account of the Parachor.

The oxidation of N-methylnicotine to hygric acid might have been included with advantage in the proof of the constitution of nicotine. The author retains the open-chain formulae for the aliphatic diazo compounds.

A number of misprints in the earlier edition have been corrected. The author writes with his accustomed clarity and presents the matter in a form which can be easily assimilated. In a book of this size, intended for honours students, and ranging over a wide field, the treatment of each subject is necessarily only an outline but the numerous references to original papers and monographs should encourage the student in the author's words "to go further."

E. W. McClelland

Colloid Aspects of Food Chemistry and Technology. By William Clayton. 25 × 15 cm; pp. vii + 563. London: J. and A. Churchill, 1932. Price: 36 shillings. Although practically every process employed in the preparation and treatment of foods presents problems in colloid chemistry, it is a surprising fact that this volume is the first attempt, so far as the reviewer is aware, to bring together the knowledge in this important field of applied science. The author is to be congratulated on having brilliantly achieved his aim to fill this gap in textbook literature. A very wide range of subjects is covered and in every case the exposition is lucid and the treatment commendably balanced.

The value of the work is much enhanced by a comprehensive list of selected references drawn both from the scientific and technical literature.

The book will be indispensable for all chemists and technologists who are concerned with the preparation or control of food products. The scope of its utility might be even wider, for I am inclined to think that the ordinary undergraduate science student would find that this work presented the essentials of colloid chemistry quite as clearly and far more entertainingly than most of the volumes on which he usually depends.

A wholly admirable production.

J. C. Drummond

Matière et Atomes. By A. Berthoud. Second Edition. 18 × 11; pp. 324. Paris: G. Doin & Cie. Price: 26 francs. This is a second edition of Professor Berthoud's "Nouvelles Conceptions de la Matière et des Atomes" first published in 1922. The earlier volume has been completely remodelled and a new chapter added dealing with wave mechanics. The result is an excellent descriptive account of the development of modern ideas about atoms and quanta. The style is clear and concise, and only the simplest mathematical knowledge is assumed. Nevertheless the more difficult topics are not avoided and the reader is enabled to apprehend the physical principles which underlie such subjects as wave mechanics and relativity.

Professor Berthoud is to be congratulated on this very readable volume; it should appeal not only to chemists but also to the general reader who wishes to learn something of the trend of scientific ideas.

S. Sugden

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten. By Carl Drucker. 24 × 17 cm; pp. xx + 234. Berlin: Verlag Chemie, 1929. Price: 24 marks. This is No. 10 of the *Abhandlungen der deutschen Bunsengesellschaft* and is a supplementary volume to No. 5. It contains chiefly data which appeared from 1914 to 1927 both inclusive. Cells in which non-electrolytes have been added are also included. The book is invaluable for reference purposes.

Wilder D. Bancroft

Errata

Make the following changes in the article by Reed and Theriault: *J. Phys. Chem.*, **35**, 673 (1931).

p. 677. Insert "t" as an exponent after 0.01 in the first equation;

p. 693. Insert equality sign between σ_1 and the radical in equation 20;

p. 964. In Equation 15 read $(5)^2$ instead of (5).

Make the following change in the article by Cullinane, Embrey and Davies: *J. Phys. Chem.*, **36**, 1434 (1932).

p. 1441. In the fifteenth line, after "hole" insert "over which filter paper was attached. The weighing bottle was fitted with a hollow ground-glass stopper containing at the side a small hole."

Make the following change in the article by Davis: *J. Phys. Chem.*, **36**, 1449 (1932).

p. 1452. In the third line from the bottom read "alkali" instead of "alumina."

THE ADSORPTION OF CATIONS FROM AMMONIACAL SOLUTION BY SILICA GEL*

BY I. M. KOLTHOFF AND V. A. STENGER

Preliminary Communication

In a note on the preparation of metallized gels, Grant W. Smith and L. H. Reyerson¹ called attention to the strong adsorption of complex ammonium ions of copper and nickel by silica gel. It seemed to us that the significance of the ammonia in the complex is of secondary order only, in so far as various cations are kept in solution by the formation of complex bases and ions. This assumption appeared to be true, as will be shown later on in this paper. A more detailed study of the adsorption of cations by silica gel from alkaline medium was of interest, also with regard to the problem of coprecipitation in analytical chemistry. Preliminary experiments showed that the adsorption of cations by hydrous oxides from alkaline medium was qualitatively determined by the same factors as the adsorption by silica gel. Since the former undergo, after their precipitation, rapid changes on aging, the use of silica gel seemed very promising for a systematic study of the factors governing this adsorption.

The exact interpretation of the results of the adsorption experiments is made very complicated owing to the highly porous structure of the silica gel. Active silica gel appeared to be fairly soluble, even in relatively weakly alkaline solutions; the solubility increasing with time of shaking. Furthermore, the adsorption equilibrium is attained very slowly due to the slow penetration of the ions into the interior of the gel, and consequently the adsorption is not reversible. During the course of the investigation various factors were found to influence the adsorption process, making a quantitative interpretation impossible. A report of the results so far obtained—although of preliminary character—is of interest, since it is possible to derive some general conclusions concerning the factors affecting the adsorption of cations from alkaline medium by silica gel.

Materials used: Silica gel: The silica gel was purchased from the Silica Gel Corporation. The particles ranged from about 1 to 2 millimeters in diameter, the shapes being irregular. The product was purified by² heating with concentrated nitric acid until the particles were clear and colorless; the gel washed with water until no acid could be detected in the wash-water, and thereafter electrolyzed for four weeks. During the last week the water added to the dialyzer did not show a change in conductivity. The product

* Contribution from the School of Chemistry of the University of Minnesota.

¹ G. W. Smith and L. H. Reyerson: *J. Am. Chem. Soc.*, **52**, 2584 (1930).

² The authors wish to thank Mr. W. J. Mitchell for his assistance in the preparation of the pure gel.

was dried first at 200° and then at 600° and kept in well-closed bottles. After heating a long time over the blast lamp a loss in weight of 3% was noticed. No acid could be detected in the gel after the electro dialysis.

Ammonia: The ammonium hydroxide used was obtained carbonate free by distillation from barium hydroxide, and kept in paraffined bottles with protection from carbon dioxide from the air. Its strength was about 4N. The other products used were C. P., and if necessary purified by repeated crystallizations.

General procedure: The solutions were made up in a 100 c.c. volumetric flask, previously freed from carbon dioxide, and transferred to a 200 c.c. Erlenmeyer flask of Pyrex glass containing a weighed amount of silica gel. The flask was stoppered and rotated for the indicated time at room temperature, usually around 25°. At the same time a blank without gel was run under the same conditions and the amount of adsorption calculated from the difference in concentrations. In many cases the gel was quickly washed with conductivity water (usually four times), and then extracted with an excess of acid. By back titration with standardized sodium hydroxide the total amount of base adsorbed was found, and the cation, whose adsorption was studied, determined in the neutralized solution. The direct determination of the amount of ammonia and cation present in the gel was of distinct advantage in cases where relatively strong ammoniacal solutions had been used.

Experimental

Adsorption of sodium hydroxide by silica gel.

TABLE I

0.5 g. of gel was left in contact with 100 c.c. sodium hydroxide solution for 40 minutes with occasional shaking by hand. (Room temperature 25°).

The amount of base adsorbed was determined by back titration of the supernatant liquid, and also by extraction of the gel with hydrochloric acid.

Original normality sodium hydroxide	Final normality	Milli eq. NaOH adsorbed per 1 g. silica gel (titration solution)	Milli eq. NaOH adsorbed per 1 g. silica gel (extract gel)
0.01	0.0079	0.424	0.37
.025	.0216	.68	.60
.05	.0458	.84	.71
.075	.0704	.90	.84
.10	.0942	1.16	1.02
.15	.144	1.20	1.11

In agreement with Patrick and Barclay³ and F. E. Bartell and Y. Fu⁴ it was found that the adsorption of sodium hydroxide takes place according to the ordinary adsorption isotherm. However, it should be mentioned that

³ Patrick and Barclay: *J. Phys. Chem.*, 29, 1400 (1925).

⁴ Bartell and Fu: *J. Phys. Chem.*, 33, 676 (1929).

the figures in Table I are more or less arbitrary; the adsorption increases with the time of standing; after 12 hours standing with occasional shaking about double the amount of base was adsorbed from the first four solutions. It seems impossible to reach the equilibrium conditions; on standing more of the gel is going into the solution, and the figures given in Table I have not been corrected for the dissolved part. After one to two days of standing all the gel went into solution in 0.1 to 0.2 N sodium hydroxide.

Adsorption of barium hydroxide by silica gel.

TABLE II

0.5 to 1 g. of gel was left in contact with 100 c.c. barium hydroxide solution for 13 to 17.5 hours, with occasional shaking by hand. Further conditions as in Table I.

Original normality barium hydroxide	Contact 13 hours 0.5 g. silica gel		Contact 17.5 hours 1 g. silica gel	
	Final norm. Ba(OH) ₂	m. eq. Ba (OH) ₂ ads. per 1 g. gel (titration solution)	Final norm. Ba(OH) ₂	m. eq. Ba (OH) ₂ ads. per 1 g. gel (titration solution)
0 002	0 00066	0 268		
005	00157	.686		
.010	.00416	1.168		
.020	.0106	1 88		
.050	.0315	3.70	0 0168	3.32
.070	.0544	3 12		
.100	.0863	2.74	.0708	2.92
.150	.1365	2.70		
.200	.1884	2.32	.176	2.40

A maximum in the adsorption is noticed in about 0.05 N barium hydroxide solution. It seems that the appearance of this maximum has to be attributed to an obstruction of the pores of the gel by the adsorbed barium hydroxide.

Adsorption of calcium hydroxide by silica gel.

TABLE III

0.5 g. of gel was left in contact with 100 c.c. calcium hydroxide solution for 17 hours with occasional shaking by hand.

Original normality of Ca(OH) ₂	Final normality of Ca(OH) ₂	m. eq. Ca(OH) ₂ ads. per 1 g. gel (titration solution)	m. eq. Ca(OH) ₂ ads. per 1 g. gel (extract gel)
0.0037	0.00097	0.562	0.56
.0093	.00252	1.354	1.42
.0187	.00442	2.86	2.48
.0281	.00995	3.58	3.70
.0375	.0155	4.40	4.26

In the last three experiments a precipitate of calcium silicate was formed.

Comparison of the results in Tables I, II, and III shows that the alkaline earth hydroxides are stronger adsorbed than sodium hydroxide. This result was to be expected considering the slight solubility of the alkaline earth silicates. Calcium hydroxide is somewhat more strongly adsorbed than barium hydroxide. The adsorption is not reversible, and the reported figures have no exact significance. It seems that the internal structure of the gel is changed during the adsorption of the hydroxides.

In the following experiments the adsorption of calcium hydroxide was determined in the presence of various concentrations of ammonia, ammonium salts, and alkali salts. Later the results will be compared with those obtained in the adsorption of copper ions in similar solutions.

The results given in Table IV show that the amount of calcium adsorbed from ammoniacal solution increases with the time of contact between the gel and the solution.

TABLE IV

0.5 g. of gel was left in contact (occasional shaking) with 100 c.c. of a solution containing 0.05 N calcium chloride and 0.5 N ammonium hydroxide. After the indicated time of standing the calcium was determined in 50 c.c. of the supernatant solution according to the oxalate method.

Time of Con- tact in hours	Final normality Ca ⁺⁺	M. eq. Ca ⁺⁺ adsorbed per 1 g. silica gel (titration solution)	Time of con- tact in hours	Final normality Ca ⁺⁺	M. eq. Ca ⁺⁺ adsorbed per 1 g. silica gel (titration solution)
4	0.0372	2.56	30	0.0288	4.25
8	0.0346	3.09	40	0.0278	4.44
12	0.0334	3.33	70	0.0252	4.97
20	0.0305	3.91	100	0.0262	4.75

Table IV shows that the adsorption increases regularly with the time of contact between solution and gel. Only in the last case (100 hours standing) was there apparently less adsorbed than after 70 hours. Special experiments showed that this deviation is to be attributed to the increasing solubility of the gel with the time of standing. After the longer time of standing it was impossible to extract the calcium quantitatively from the gel with an excess of acid. The pores of the gel were obstructed by the calcium silicate formed and the diffusion of the acid into the interior of the gel was strongly inhibited.

In order to get reproducible results it is necessary to treat solutions and gel under exactly the same conditions.

In the study of the influence of the concentration of ammonia upon the adsorption of the calcium hydroxide, 0.5 to 1 g. of the gel was *shaken* at uniform speed with a calcium chloride solution, containing various concentrations of ammonia.

The adsorption of the calcium reaches a maximum in about 1 N ammonium hydroxide solution. A special study was made of the complex cation formation between calcium ions and ammonia; no indication was obtained of the existence of that type of complex ions. The results of this study will be re-

TABLE V

0.5 to 1 g. gel shaken for 21 hours with 100 c.c. solution containing 0.05 N calcium chloride and various concentrations of ammonia. Amount of calcium adsorbed determined in 50 cc. supernatant liquid by the oxalate method.

Grams silica gel used	Concentration ammonia added	Final normality Ca^{++}	M. eq. Ca adsorbed per 1 g. gel (titration solution)
1	0	0.0498	0.02
1	0.001	.0450	.50
1	.01	.0416	.84
0.5	.05	.0372	2.55
1	.10	.0241	2.59
1	.50	.0130	3.70
1	1.00	.0129	3.71
0.5	1.00	.0292	4.15
0.5	2.00	.03395	3.21
1	5.00	.0301	1.99

ported in a later paper; they show that the effect of the concentration of the ammonia upon the calcium adsorption cannot be explained in terms of the formation of an ammonio complex. The ammonia has a replacing effect upon the adsorbed calcium ions; with increasing ammonia concentration the ratio NH_4OH to $\text{Ca}(\text{OH})_2$ adsorbed increases regularly as is shown by experiments reported in Table VI.

The amount of calcium adsorbed was determined by analysis of the solution. It was impossible to extract all calcium from the gel with dilute acid, and the figures given in the table are considerably in error and placed between parentheses. However, it was possible to extract practically all ammonia from the gel, and from the total basicity of the extract and its calcium content the amount of ammonia adsorbed could be calculated. These figures are more reliable than those found in the titration of the supernatant liquid of the gel, especially in the more concentrated ammonia solutions; therefore the latter are given between parenthesis. In the calculation of the ratio *moles* NH_4OH : $\text{Ca}(\text{OH})_2$ adsorbed the figures in the eight and fifth columns have been used.

The figures in Table VI are not strictly comparable with those in Table V. because in Table VI a mixture of the two hydroxides was used and the hydroxyl ion concentration was much larger than in the mixtures used in Table V. The replacing effect of the ammonium hydroxide in the experiments of Table VI is quite evident, in spite of the fact that the adsorption of calcium hydroxide was made more favorable.

In Table VII the effect of the presence of ammonium, sodium and potassium salts on the adsorption of calcium at various ammonia concentrations is given. Alkali salts decrease the adsorption of calcium, owing to their partial replacement of this ion at the surfaces of the silica gel. Ammonium salts exert a similar influence, but in addition decrease the hydroxyl ion concentration of the solution, and therefore their effect upon the calcium adsorption is larger than that of sodium or potassium salts.

TABLE VI

0.5 g. of silica gel in contact with a mixture of calcium and ammonium hydroxide for 2 hours with occasional shaking.									
Original normality Ca(OH)_2	Original normality NH_4OH	Final normality Ca(OH)_2 (oxalate method)	Final normality NH_4OH	M. eq. Ca^{++} adsorbed per 1 g. gel (titration solution)	M. eq. Ca adsorbed per 1 g. gel (extract)	M. eq. NH_4OH adsorbed (solution)	M. eq. NH_4OH adsorbed extract (gel)	M. eq. NH_4OH adsorbed $\text{NH}_4\text{OH}:\text{Ca(OH)}_2$	Molar ratio adsorbed
0.0033	0	0.00219	0	0.022	(0.220)	—	—	—	—
.0083	0	.00547	0	.566	(.576)	—	—	—	—
.0165	0	.0102	0	1.26	(1.10)	—	—	—	—
.0165	0.05	.0069	0.0488	1.92	(1.37)	(0.24)	.294	.306	.656
.0165	.10	.00715	.097	1.87	(1.17)	(.60)	.614	1.44	1.93
.0165	.50	.00703	.4897	1.90	(0.98)	(1.06)	1.37	2.27	2.44
.0165	1.00	.00619	.9788	2.06	(0.86)	(2.24)	1.99	2.98	2.84
.0165	2.00	.00721	1.968	1.86	(0.69)	(2.4)	2.27	2.44	2.84
.0165	3.00	.00603	2.946	2.10	(0.64)	(4.0)	2.98	2.84	2.84

TABLE VII

0.5 to 1 g. of silica gel was shaken for 21 hours with solutions containing 0.05 N calcium chloride and the indicated amounts of other constituents

Grams gel taken	Original normality ammonia	Kind and concentration salt added	Final normality calcium	M. equivalents Ca^{++} adsorbed per 1 g. gel
1.0	0.01	0	0.04165	0.835
1.0	.01	0.01 N NH_4Cl	0.04235	.775
0.5	.05	0	.03725	2.55
.5	.05	0.1 N NH_4Cl	0.04478	1.044
.5	.05	1 N NH_4Cl	.0500	0.0
.5	.05	0.1 N KCl	.0393	2.14
.5	.05	1 N KCl	0.04335	1.33
.5	.05	1 N NaCl	.04375	1.27
.5	.5	0	.03255	3.49
.5	.5	0.1 N NH_4Cl	.0364	2.72
.5	.5	1 N NH_4Cl	.0473	0.54
.5	1.0	0	.02925	4.15
.5	1.0	0.1 N NH_4Cl	.0326	3.48
.5	1.0	1 N NH_4Cl	0.0462	0.76
.5	1.0	1 N KCl	.0442	1.16
.5	1.07	1 N NH_4Cl	.04478	1.04
.5	1.07	1 N NH_4NO_3	.04483	1.03
.5	4.0	0	.0416	1.68
.5	4.0	1 N NH_4Cl	.042	1.60

Adsorption of copper from ammoniacal solution.

Silica gel shaken with an ammoniacal copper solution assumes immediately an intense dark blue color, indicating the adsorption of the ammonio copper ion. As in all other cases the amount of copper adsorbed increases with the time of shaking of the solution with the gel.

In the following experiments two types of copper solutions have been used.

Solution A: Hydrous copper oxide was precipitated by adding a recrystallized copper sulfate solution to a slight excess of ammonia. The precipitate was washed with distilled water until the washings were no longer basic to phenolphthalein and then treated with a solution containing 1.5 N ammonia. Part of the precipitate dissolved with the formation of the dark blue solution, (the undissolved part was shown to be free of sulfate) containing 0.05 molar copper, 0.03 molar sulfate and 1.313 N ammonia. It was considered to be equivalent to a mixture of 0.05 molar $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$; 0.030 molar ammonium sulfate and 1.052 N ammonia in excess. This solution and some of its dilutions have been used in the experiments.

Solution B: The undissolved part of the hydrous copper oxide from the previous treatment was shaken with 1.5 N ammonia, the solution becoming only a faint blue. In order to increase the solubility of the ammonio copper hydroxide it was necessary to add some ammonium salt. The final solution

obtained contained 0.0261 molar copper as $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$; 0.02 molar ammonium chloride and 1.064 N ammonia in excess.

It may be mentioned here that all copper solutions used contained some ammonium salts; since the latter decrease the hydroxyl ion concentration markedly, the adsorption experiments are not strictly comparable with those obtained in a mixture of calcium chloride and ammonia, to which no ammonium salt had been added.

In Table VIII it is shown that the adsorption of copper from ammoniacal solution increases with the time of shaking. In the first six and the last six experiments the copper content was determined in 25 cc. of the supernatant liquid after 2, 6, and 24 hours shaking respectively and after 24, 49 and 90 hours shaking respectively. From the difference in concentration the amount of copper adsorbed was calculated. The figures so obtained have no exact significance, since part of the gel went into solution. In some cases the gel after extraction of the copper was collected and weighed after ignition over the blast lamp. In this way the actual amount of copper adsorbed per 1 g. of gel was found; the figures are given in the last column of Table VIII. Those corrected figures are markedly higher than those calculated with the assumption that the silica gel remained unchanged. The relative change in the adsorption is approximately the same in both columns.

TABLE VIII

0.25 g. silica gel was shaken with a copper solution prepared by diluting various amounts of solution B to 100 c.c., with or without addition of more NH_4OH . 0.5 g. silica gel was shaken with solution B undiluted. After various times the solutions were analyzed for copper iodometrically.

Grams of gel	Time of shaking in hours	Original molarity Cu^{++}	Original normality NH_4Cl	Excess of NH_4OH (normality)	Milli-eq. Cu^{++} adsorbed per 1 g. gel	Milli-eq. Cu^{++} adsorbed (Corrected for solubility of gel.)
0.25	2	0.0130	0.01	0.532	2.44	
0.25	6	0.0130	0.01	0.532	3.64	
0.25	24	0.0130	0.01	0.532	4.44	
0.25	24	0.0130	0.01	0.532	4.04	
0.25	49	0.0130	0.01	0.532	5.42	
0.25	90	0.0130	0.01	0.532	5.64	7.67
0.25	24	0.0147	0.01	1.12	3.61	5.29
0.25	24	0.0147	0.01	1.73	3.25	5.41
0.25	24	0.0147	0.01	2.34	2.43	4.55
0.25	24	0.0147	0.02	1.12	3.47	4.78
0.5	2	0.0261	0.02	1.064	2.74	
0.5	6	0.0261	0.02	1.064	3.22	
0.5	24	0.0261	0.02	1.064	3.88	
0.5	24	0.0261	0.02	1.064	3.90	
0.5	49	0.0261	0.02	1.064	4.45	
0.5	90	0.0261	0.02	1.064	4.61	6.19

Similar experiments as described in Table VIII have been made with copper solution A. Some of the results are given in Table IX.

TABLE IX

0.5 g. silica gel was shaken with 100 c.c. of diluted copper solution A, pipetting out 25 cc. after 2, 6, and 24 hours shaking, respectively.

Time of shaking in hours	Original molarity Cu ⁺⁺	Original normality (NH ₄) ₂ SO ₄	Excess of NH ₃ (normality)	Milli eq. Cu ⁺⁺ per 1 g. gel (uncorrected for solubility gel.)
2	0.0251	0.03	0.526	2.14
6 2/3	.0251	.03	.526	3.22
24 2/3	.0251	.03	.526	4.08
2	.0250	.05	.500	2.34
6	.0250	.05	.500	2.82
24	.0250	.05	.500	3.59
2	.050	.06	1.052	1.82
6	.050	.06	1.052	2.26
24	.050	.06	1.052	3.67

The results of Tables VIII and IX show that even after a few days of shaking the adsorption equilibrium is not yet established. In order to get comparable results in the study of the influence of various factors upon the adsorption of copper from ammoniacal solution, it is necessary to work under the same experimental conditions.

The results in the following table show that the adsorption of copper first increases with increasing ammonia concentration, reaches a maximum and decreases thereafter with increasing ammonia concentrations. In order to be able to work at low ammonia concentrations, copper solutions with a higher ammonium salt content were used. 10 c.c. 0.5 molar copper sulfate were mixed with various amounts of 0.5 N ammonia and diluted in a volumetric flask to 100 c.c. The solutions were analyzed for copper and total ammonia content. In the expression of the concentration of the excess of ammonia it was assumed that the copper was present in the form of Cu(NH₃)₄(OH)₂ or of Cu(NH₃)₄⁺⁺.

TABLE X

0.5 g. silica gel with 100 c.c. copper solution, containing 0.025 molar copper and 0.025 molar ammonium sulfate; occasionally shaken for 12 hours and thereupon mechanically shaken for 3 hours.

Normality of NH ₃ in excess	Final molarity Cu	Milli eq. Cu adsorbed per 1 g. gel	Normality of NH ₃ in excess	Final molarity Cu	Milli eq. Cu adsorbed per 1 g. gel
0.05	0.0173	3.08	.40	.0165	3.38
.10	.0163	3.45	.90	.0180	2.80
.15	.0150	4.01	1.00	.0181	2.76
.20	.0141	4.36	4.00	.0196	2.15

The location of the maximum also depends upon the concentration of ammonium salt present; for this reason the results are not directly comparable with those in Table V on the adsorption of calcium.

Table XI shows that potassium chloride and ammonium salts have a similar effect upon the adsorption of copper from ammoniacal solution as upon that of calcium (compare Table VII).

TABLE XI

0.5 g. silica gel with 100 c.c. copper solution containing 0.025 molar copper and 0.025 molar ammonium sulfate; occasionally shaken for 12 hours and thereupon mechanically shaken for 3 hours.

Normality excess NH_3	Kind and normality of salt added	Final molarity copper	Milli eq. Cu adsorbed per 1 g. gel
0.05	—	0.0173	3.08
.05	.05 N NH_4Cl	.0172	3.12
.05	.5 N NH_4Cl	.0210	1.62
.10	—	.0163	3.45
.10	.05 N NH_4Cl	.0164	3.41
.10	.5 N NH_4Cl	.0215	1.38
.10	.5 N KCl	.0178	2.88
.20	—	.0141	4.36
.20	.5 N NH_4Cl	.0210	1.58
.20	.5 N NH_4NO_3	.0211	1.54
1.0	—	.0181	2.76
1.0	1 N NH_4Cl	.0240	0.38
4.0	—	.0196	2.15
4.0	1 N NH_4Cl	.0249	0.04

It was of interest to determine the molecular ratio of adsorbed ammonia and copper. If the copper cation would be adsorbed as the ammonio complex $\text{Cu}(\text{NH}_3)_4^{++}$, this ratio should be higher than 4:1, since some ammonia is adsorbed simultaneously with the copper. As Table XII shows, the ratio is decidedly lower than 4, indicating that part of the copper is adsorbed as aquo ion and part as ammonio ion, or that originally the ammonio complex is adsorbed, splitting off ammonia after the adsorption. The decrease in the ratio of adsorbed ammonia and copper with the time of shaking is in harmony with the latter assumption. More experiments will be made before definite conclusions can be drawn.

Reversibility of the adsorption:

Several experiments showed that neither the adsorption of the calcium nor that of copper is reversible. If a gel having copper and ammonia adsorbed is washed with water for long periods of time, part of the ammonia goes into solution; the copper remains in the gel and even with the sensitive ferrocyanide reagent its presence cannot be detected in the solution. A gel, which had been

TABLE XII

0.25 to 0.5 g. silica gel was shaken for 24 hours with 100 c.c. copper solution A or B. The residue was quickly washed four times with water, and treated with an excess of standardized sulfuric acid, until the gel was colorless. The solution was back titrated with sodium hydroxide, thus giving the total amount of base adsorbed. The copper content of the original filtrate was determined in an iodometric way.

Normality excess NH ₃	Normality ammonium salt	Original molarity copper solution	Milli eq. NH ₃ adsorbed	Milli eq. Cu adsorbed	Molar ratio (NH ₃):(Cu) adsorbed
0.532	0.01 N NH ₄ Cl	0.013	5.29	3.83	2.76
1.064	0.02 N NH ₄ Cl	0.0261	5.65	3.43	3.29
0.782	0.01 N NH ₄ Cl	0.013	5.02	3.28	3.06
0.500	0.05 N (NH ₄) ₂ SO ₄	0.025	5.13	3.01	3.40
0.526	0.03 N (NH ₄) ₂ SO ₄	0.025	5.14	4.06	2.53
1.052	0.06 N (NH ₄) ₂ SO ₄	0.050	6.15	3.72	3.30

shaken for 90 hours with an ammoniacal copper solution, was treated with 10 c.c. 5.0 N ammonium chloride for three days. Although the ammonium salt decreases the adsorption of copper very much (compare Table XI), it only replaced 25% of the copper from the gel after the metal ion had been adsorbed. Under similar conditions potassium chloride did not replace any copper from the gel. The ammonia content of the gel, however, decreased very much, thus decreasing the ratio of NH₃ to Cu present in the gel. This again may indicate that the copper originally is adsorbed as ammonio ion, which can split off the ammonia held in complex form. Such experiments, however, do not yield a definite proof that originally the complex copper ion is adsorbed, as the speed of adsorption and desorption of ammonia may be much larger than that of the copper ion.

It may be mentioned that it is very hard to remove all the copper from a gel, after it has been shaken for a longer time (90 hours) with an ammoniacal copper solution. Even after continuous extraction for 6 months with cold and hot mixtures of sulfuric and nitric acid some copper was present in the interior of the gel.

Discussion: The experiments described in this paper revealed various difficulties making an exact interpretation of the results impossible. Various factors hereunder mentioned, affecting the adsorption, will be made the subject of a more detailed investigation:

1. Silica gel dissolves in alkaline solution.
2. By the aggressive action of the solvent, the outside and internal surface of the gel may change during the experiment.
3. The adsorption equilibrium is reached very slowly; even after shaking for a few days the maximum in the adsorption-time curve is not reached in many cases.

4. After shaking the gel for a long time with the solution, it seems impossible to extract divalent cations entirely from the gel, even upon treatment with strong acids.

5. The pores of the gel may be obstructed by the adsorbed ions, owing to a formation of insoluble silicates in the capillaries. (Ca;Cu).

6. The adsorption process is not reversible.

7. The speed of adsorption (diffusion into the interior of the gel) and desorption may be different for different ions and molecules. Thus it seems that ammonia is much faster adsorbed and desorbed than calcium and copper.

In the literature on the adsorption of ions and molecules by silica gel, these various factors have not been considered, and it is possible that the conclusions inferred need some correction.

In spite of the difficulties mentioned, the following conclusions may be drawn from the present study:

The adsorption of cations from alkaline solution by silica gel is a secondary adsorption; the hydroxyl ions being primarily adsorbed, dragging an equivalent amount of cations to the surface. Therefore, the adsorption will increase with increasing hydroxyl ion concentration. The adsorption of a cation salt in ammoniacal medium first will increase with the ammonia concentration as a consequence of the increase of the hydroxyl ion concentration. However, the ammonia being a base itself, is also adsorbed by the gel and has a replacing effect upon the adsorbed cation. Therefore, quite generally a maximum in the adsorption of any cation will be observed at a certain ammonia concentration, and the cation adsorption will decrease at higher ammonia concentrations. It seems that this behavior is not specific for adsorptions by silica gel; hydrous oxides like those of aluminum and ferric iron behave in a similar way. In the literature this maximum in the adsorption of cations by hydrous oxides at a certain ammonia concentration is always connected with complex formations between the cation and ammonia; this, however, is only a circumstantial coincidence and does not explain the experimental facts. The adsorption of cations by hydrous oxides resembles that by silica gel very closely, as will be shown in future papers.

The addition of ammonium salts to the ammoniacal solutions decreases the adsorption of calcium and copper for two reasons. In the first place, the ammonium ions decrease the hydroxyl ion concentration, and, in the second place, they have a replacing effect upon the adsorbed calcium and copper. This last effect is also exerted by sodium and potassium salts, which decrease the adsorption of calcium and copper from ammoniacal solution.

It has been mentioned in this paper that calcium does not form an ammonio ion, and therefore is adsorbed as aquo calcium ion. The adsorption of copper from ammoniacal solution is quite similar to that of calcium; the main function of the ammonia being the prevention of the precipitation of the copper cations from the solution. An ammoniacal copper solution contains few aquo copper ions; if the latter were soluble in alkaline medium, they would be adsorbed as well as the ammonio copper ions. This was proved by the following experiments:

Silica gel was treated with an alkaline copper salicylate solution. In such a solution most of the copper is firmly bound as a complex copper salicylate anion, which will not be adsorbed. Only few aquo copper cations can be present in the solution. On shaking of the silica gel with the alkaline copper salicylate, the gel assumed a light bluish color by the adsorption of copper. The gel was washed with water for a long time in order to remove any salicylate which had diffused into the interior of the gel; the latter did not give off any copper during the washing process. The washed gel was extracted with sulfuric acid, thus bringing all the copper into the solution. The latter and the gel were shaken out with ether, and the ethereal extract evaporated at room temperature. No salicylic acid could be detected in the residue, showing that the copper had been adsorbed as aquo cation. The copper content in the acid extract was determined iodometrically. Since the aquo copper ion concentration in the alkaline salicylate solution is extremely small, the amount of copper adsorbed by the gel is also very small. This is shown by the figures in Table XIII.

TABLE XIII

Adsorption of copper from alkaline copper salicylate solution. Copper salicylate was prepared by mixing equivalent amounts of pure copper sulfate and sodium salicylate. The crystals formed were collected, washed, and dried in the air. 20 grams of the crystals were treated with 10 grams of sodium salicylate (roughly the quantity needed to form $\text{Na}_2\text{Cu}(\text{Sal})_4$), 20 grams anhydrous sodium carbonate and diluted with water to 500 c.c. The copper content of the solution was 0.1155 molar, 25 c.c. of this solution was diluted with water to 100 c.c. and shaken with 0.5 g. silica gel for 2 hours.

Addition to copper salicylate solution	M. equivalents Cu adsorbed per 1 g. gel (titration solution)	M. equivalents Cu adsorbed per 1 g. gel (extract gel)
—	0.172	0.186
1.05 g. NaHCO_3	.075	.090
5 g. Na_2CO_3	.264	.264
0.5 g. salicylic acid	.108	.100

If the washed bluish gel, containing the copper as aquo cation was shaken with a dilute ammonia solution, it immediately assumed a dark blue appearance as a result of the formation of the ammonio copper ion. It is quite possible that the latter is more strongly adsorbed than the aquo copper ion. The last experiment, however, does not prove this point. The conclusion seems warranted that the strong adsorption of copper from ammoniacal solution takes place by virtue of the fact that the metal can exist as cation in this alkaline medium, and not because the ammonio ion is so much more strongly adsorbed than the aquo ion. The fact that the adsorption of calcium, which does not form ammonio ions, is similar to that of copper from ammoniacal solution justifies the above conclusion.

Summary

1. The study of the adsorption of cations from alkaline solutions is complicated by the facts, that the gel dissolves even in dilute alkali, changing its structure during the experiment, that the adsorption equilibrium is reached very slowly, the adsorption process is not reversible, that the pores of the gel may be obstructed by formation of insoluble silicates, and that the speed of adsorption and desorption of various ions and molecules may be different.

2. The adsorption of calcium and copper from ammoniacal solutions shows a similar character in spite of the fact that the calcium is adsorbed as aquo ion, the copper as ammonio ion. In the latter case the ratio of NH_3 to Cu present in the gel, however, is always smaller than 4:1.

3. The adsorption of calcium and copper from ammoniacal solution first increases with the ammonia concentration until a maximum is reached. At larger ammonia concentrations the adsorption decreases, owing to the fact that the replacing action of the ammonia upon the adsorption of the cations has a larger effect than the increase of the hydroxyl ion concentration.

4. Ammonium salts decrease the adsorption of calcium and copper by silica gel, because they decrease the hydroxyl ion concentration and the ammonium ions have a replacing effect upon the adsorption of the cations mentioned. Potassium and sodium salts have a similar replacing effect.

*Minneapolis, Minnesota,
May 16, 1932.*

THE HEAT CAPACITY AND FREE ENERGY OF FORMATION OF ETHYLENE GAS*

BY MATTHIAS E. HAAS WITH GEBHARD STEGEMAN

Thermal data of the required accuracy are frequently lacking when it is desired to calculate the free energy of a given chemical reaction that is carried out under isothermal conditions. The minimum data required for such a calculation are: (1) the heat capacities of all the substances involved in the reaction for the particular range of temperature for which the heat capacities hold; (2) the heat of reaction at some temperature within this temperature range; and (3) one value of the free energy of the reaction within the range of temperature for which the heat capacities are valid.

The determination of the heat capacity of ethylene gas through the temperature range 0° to 70°C., constitutes the experimental part of this investigation. The other required data for the computation of the free energy of formation of ethylene gas are taken from the work of other investigators.

Partington and Shilling¹ give a good account of the work on ethylene gas. The most recent determinations are given in Table I.

TABLE I

	Temperature	C _p
Scholer (1914)	20°C.	10.007
Schweikert (1915)	0	10.267
Scheel and Heuse (1919) ²	18	10.22
	-36	9.19
	-68	8.81
	-91	8.65
	12	10.25
Dixon and Greenwood (1924) ³	41.5	10.57
	63.5	10.84
	89.0	11.14

The Flow Method. The constant-flow method was used in this investigation. This method is fully described by previous investigators.^{4,5} The apparatus was reconstructed after the completion of a similar problem on ethane gas,⁵ and certain modifications were introduced.

* Contribution No. 242 from the Department of Chemistry, University of Pittsburgh.

¹ Partington and Shilling: "The Specific Heats of Gases," 195 (1924).

² Scheel and Heuse: Ann. Physik, 59, 86-94 (1919).

³ Dixon and Greenwood: Proc. Roy. Soc., 105A, 199 (1924).

⁴ Scheel and Heuse: Ann. Physik, 37, 79 (1912); 40, 473, (1913); 59, 86 (1919).

⁵ Victor R. Thayer: J. Phys. Chem., 35, 1505-1511 (1931).

Modifications. Six stopcocks were added in the specific heat apparatus, so as to facilitate the evacuation of the apparatus prior to introducing the purified gas. Mercury seals that were either movable, or that had some movable part operating in them, were extended in length so as to form a barometer column when the system was evacuated. A differential manometer containing mercury was inserted across the rate of flow device to give indication of any appreciable pressure changes during the pumping. The mercury seal in the calorimeter was replaced by a heavy-grease seal. The calorimeter lead-in tubing was lengthened by four feet to insure efficient heat transfer between calorimeter and bath.

A gear-and-chain drive was substituted for the pulley-and-belt transmission in the gas-circulating pump. In the earlier part of the work, considerable trouble was experienced due to failure or slippage in this driving mechanism. This defect was completely corrected and the rate of circulating gas was more constant than before.

A new constant-temperature bath, with redesigned thermoregulator of the toluene-mercury type, electrical heaters, relay, etc., was installed. The bath consisted of a 14 × 42 inches deep cylindrical, stoneware tank, with a lagging of double layer heavy hair felt, suitably enclosed in a case. With this equipment, it was not unusual to keep the temperature of the bath constant to 0.001° for eight to twelve hours.

The electrical equipment was similar to that used by Thayer.⁵ A 25-ohm coil, certified by the Bureau of Standards, was the ultimate standard. A Weston cell served to standardize the potential measurements, and this unit was frequently checked against the 25-ohm coil and also against a standard resistance thermometer. A White Double Potentiometer was used for measuring all e.m.f.'s. The electrical heater in the calorimeter was checked for its resistance at least once for each temperature; in most of the determinations, however, this was done after each flow measurement. The physical constants of the two platinum resistance thermometers in the calorimeter were redetermined.

Purity of Ethylene. The ethylene gas used in this investigation was supplied by the Ohio Chemical and Manufacturing Company of Cleveland. Its purity, by the bromine adsorption test, was given as 99.8 per cent. Considering that this product is used in anesthesia, its high degree of purity and its freedom from toxic components must be assured to the consumer. The cylinder gas was further treated by passing it slowly over solid potassium hydroxide, phosphorus pentoxide and glass wool. It was then liquefied and solidified, pumped free from dissolved gases, and twice fractionated.

Experimental Results. The results of the heat capacity measurements are summarized in Table II. The mean specific heats recorded therein are based on at least three, and in most of the determinations, on seven to ten values for each temperature. Excepting the last two temperatures, the measurements apply to two, or three, and, at 46° to four different samples of gas.

TABLE II
Summary of Experimental Data

Temperature, °C	Specific Heat in Watt Seconds per Gram	Specific Heat in Cals. per Mol
2.50	1.4515	9.73
25.00	1.4998	10.05
31.50	1.5154	10.16
37.20	1.5375	10.31
46.00	1.5625	10.47
61.00	1.6131	10.81
66.80	1.6470	11.04

The heat loss factor of the vacuum-jacketed calorimeter was $k = 0.000046$.

Heat Capacity Equation. The molal specific heats listed in Table I were used for formulating an equation for the heat capacity of ethylene gas. This is given by

$$C_p = 4.064 + 0.02022 T.$$

For the sake of comparison, the data of Dixon and Greenwood,³ of Scheel and Heuse,² and of all investigators mentioned in Partington and Shilling,¹ were transformed into equations of the above form, and these equations were used for computing specific heats for the temperatures mentioned in Table II. The results are given in Table III. The values under "experimental" are reproduced from the foregoing table; and under "calculated" are given the values resulting from the application of the various heat capacity equations to the experimental temperatures.

Experimental		TABLE III Calculated C_p			
Temp. °K	C_p Authors	Authors	D & G	S & H	Others
275.6	9.73	9.64	10.13	9.90	9.96
298.0	10.05	10.09	10.39	10.23	10.40
304.5	10.16	10.22	10.46	10.33	10.53
310.0	10.31	10.33	10.53	10.41	10.64
319.0	10.47	10.51	10.63	10.54	10.81
334.0	10.81	10.82	10.80	10.76	11.10
340.0	11.04	10.94	10.87	10.85	11.22

Fig. 1 shows the experimental specific heat values of Scheel and Heuse, of Dixon and Greenwood, and of this investigation, the last being expressed by the straight line.

Free Energy of Formation of Ethylene Gas. The free energy of formation of one mol of ethylene gas from the elements was calculated by the general free energy equation:

$$\Delta F = \Delta H_0 - \Delta G_0 T \ln T - \frac{1}{2} \Delta G_1 T^2 - \dots + I T$$

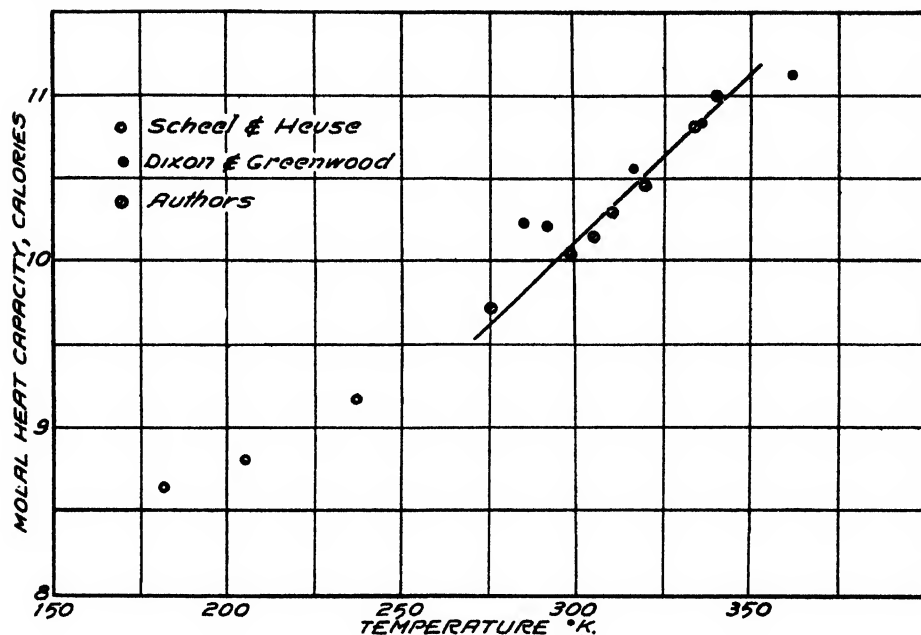


FIG. 1
Molal Heat Capacity of Ethylene

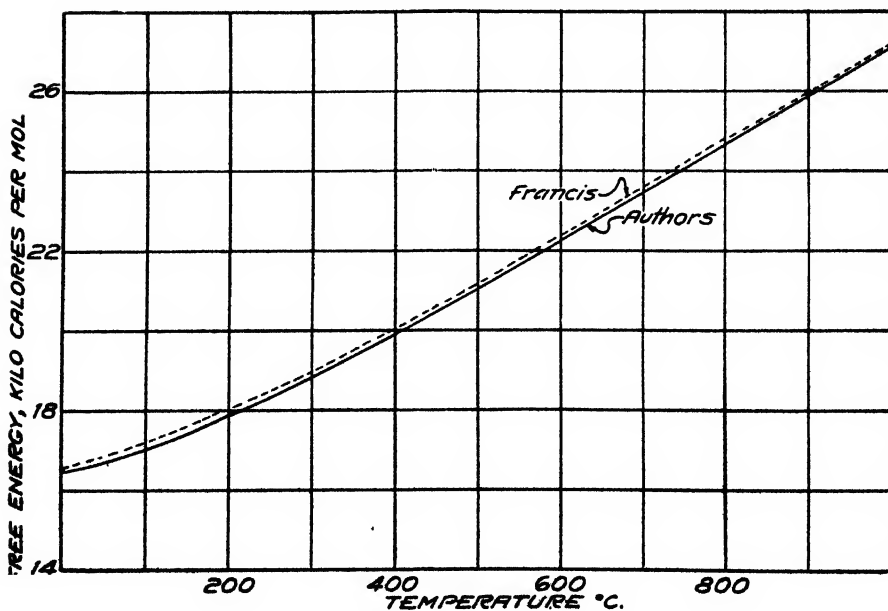


FIG. 2
Free Energy of Formation of Ethylene Gas

in which the constants ΔH_0 , Γ_0 , and Γ_1 are defined by the equations:

$$\begin{aligned}\Delta H &= \Delta H_0 + \Delta \Gamma_0 T + \frac{1}{2} \Delta \Gamma_1 T^2 + \dots \dots \dots \\ \Delta C_p &= \Delta \Gamma_0 + \Delta \Gamma_1 T + \dots \dots \dots \\ C_p &= \Gamma_0 + \Gamma_1 T + \dots \dots \dots\end{aligned}$$

The values of $\Delta \Gamma_0$ and $\Delta \Gamma_1$ are obtained from the heat capacity equations for the reactants⁶ and the resultant⁷ of the chemical reaction:

$2 \text{ C (graphite)} + 2 \text{ H}_2 = \text{C}_2\text{H}_4$, as follows:

$$\begin{aligned}2 \text{ C, } C_p &= 2 (1.1 + 0.004 T) \\ 2 \text{ H}_2, C_p &= 2 (6.65 + 0.0007 T) \\ \text{C}_2\text{H}_4, C_p &= 4.064 + 0.02022 T\end{aligned}$$

from which, by taking the reactants as negative and the resultant as positive,

$$\Delta C_p = -11.436 + 0.0108 T.$$

Using the value of ΔH_{298} as calculated by Francis,⁶ namely, $\Delta H = 14,865$ calories, the equation for the heat of reaction becomes

$$14,865 = \Delta H_0 - 11.436 (298) + 0.0054 (298)^2,$$

from which $\Delta H_0 = 17,790$.

Substituting in the free energy equation, gives

$$\Delta F = 17,790 + 11.436 T \ln T - 0.0054 T^2 + \dots \dots + I T.$$

The constant I was calculated from the equilibrium data of Pring and Fairlie⁸ in the same way as was done by Francis. The average of three values gave -67.6 . When introduced into the equation above, the free energy of formation of ethylene gas is given by

$$\Delta F = 17,790 + 11.436 T \ln T - 0.0054 T^2 - 67.6 T.$$

Fig. 2 represents the free energy expression between 0° and 1000°C . The equation calculated by Francis from the data in the literature, shows close agreement with the results of this investigation.

The experimental specific heats reported in this work are considered to be accurate within one per cent.

The writers wish to express appreciation to the United States Bureau of Mines, Pittsburgh Experimental Station, for the loan of equipment, and to Dr. A. G. Loomis and Dr. Victor R. Thayer for suggestions and criticisms in this investigation.

⁶ A. W. Francis: Ind. Eng. Chem., 20, 277-279 (1928).

⁷ This investigation.

⁸ Pring and Fairlie: J. Ind. Eng. Chem., 4, 812, (1912).

Summary

Apparatus has been reconstructed with modifications, for the purpose of determining the specific heats of gases at atmospheric pressure by the Constant-Flow Method.

Measurements of the specific heats of ethylene gas at seven temperatures, from 0° to 70°C. have been made. The equation formulated from the results is given by

$$C_p = 4.064 + 0.02022 T.$$

The free energy of formation of ethylene gas has been computed, using the specific heat equation given above.

CHEMICAL ACTION IN THE GLOW DISCHARGE

IX. Reaction in the Crookes Dark Space and Negative Glow*

BY A. KEITH BREWER AND P. D. KUECK

In the previous articles of this series it has been shown that an Electrochemical Equivalence Law, analogous to Faraday's Law for Electrolytes, holds for the chemical action in the electric discharge in gases. The definiteness of this law combined with the facts that the active states are easily identified, and that the reaction takes place in the gas phase without the presence of solvent, surface, or catalyst, makes the glow discharge an extremely fertile field for the study of chemical reactivity.

The principal difficulty at present in this type of research results from a lack of understanding of the physics of the discharge. Until this is solved an accurate estimation of the ratio of molecules formed to reactive centers (M/N) cannot be given. The present research was undertaken to clear up the uncertainty regarding the relative ability of the various regions of the discharge to incite reactivity, special attention being given to the Crookes dark space and to the negative glow. Also, a new method is suggested which permits a more accurate estimation of the number of positive ions formed than has heretofore been possible.

The Reaction

The reaction chosen for this work was the synthesis of nitrogen dioxide from an $N_2/2O_2$ mixture since the previous study of this reaction¹ yielded very clean cut results with no apparent complication. The technique was identical to that employed in the previous study.

The Method

The method of procedure employed was to measure the reactivity when various portions of the discharge were eliminated by moving the anode towards the cathode.

In the glow discharge as the anode is moved through the positive column toward the cathode the rate of change of potential between the electrodes is constant until the anode reaches the Faraday dark space where the change in potential per cm. is usually slightly increased. As soon as the anode enters the negative glow, however, no change in potential between the electrodes is observed until it has reached a point near the edge of the Crookes dark space, where the voltage rises suddenly, changing from about 300 for the average discharge to many thousand in a very short distance. The conditions

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¹ J. W. Westhaver and A. K. Brewer: *J. Phys. Chem.*, **34**, 554 (1930).

existing in the discharge when the anode has reached the edge of the Crookes dark space are identical to those found in the gas-filled x-ray tube, similar voltages being necessary to maintain the current.

From these considerations it will be seen that no difficulty is to be expected in measuring the reactivity in various regions of the discharge by changing the electrode separation until the anode approaches close to the edge of the Crookes dark space where the cathode fall of potential is no longer characteristic of the ordinary type of discharge.

Apparatus

The discharge tube is illustrated in the insert in Fig. 1. It consisted of a Pyrex tube 3.5 cm. inside diameter and 20 cm. long sealed to a 3 liter bulb. The cathode was made of an aluminum block turned to fit tightly into the bottom of the tube in order to confine the discharge entirely to the top surface. The position of the anode was adjusted by a stopcock suspension. The anode itself was made of two thin aluminum discs placed 0.5 mm. apart. The lower disc was 3.5 cm. in diameter with a 1 cm. hole in the center; the upper disc was a solid plate 2.5 cm. in diameter. It was found necessary that the outer disc fit the walls of the tube tightly to prevent the discharge from passing up along the walls when the anode approached the Crookes dark space. The 0.5 mm. separation between the plates was to allow fresh gas to diffuse into the discharge.

The rates were measured at 0.3 mm. pressure with the electrode separations from 0.2 cm. to 2.5 cm. The discharge current was maintained at 5.0 m.a. The dark space measurements were made visually with a 2.5 cm. electrode separation, the distance between the cathode and the edge of the negative glow being taken as the dark space. The electrode separation, however, has no effect on the length of the dark space.

Results

The pressure vs. time curves for the various electrode separations are given in Fig. 1. The data show a decrease in the rate of reaction as the anode approaches the cathode. Especially it should be noted that there exists a definite pressure at which the rate becomes zero for each electrode separation; this pressure decreases for increasing separation. Further, the curves show that the reaction in each instance dropped to a negligible value when the dark space approached close to the anode.

The voltage curve for various electrode separations are shown in Fig. 2. The curves become practically asymptotic to the voltage axis where the dark space reached the anode. This is the same point at which the reaction rate became negligible.

The reactivity, however, never entirely ceased as it was not possible to confine the discharge completely between the electrodes. When the electrode separation was just slightly greater than the length of dark space the high

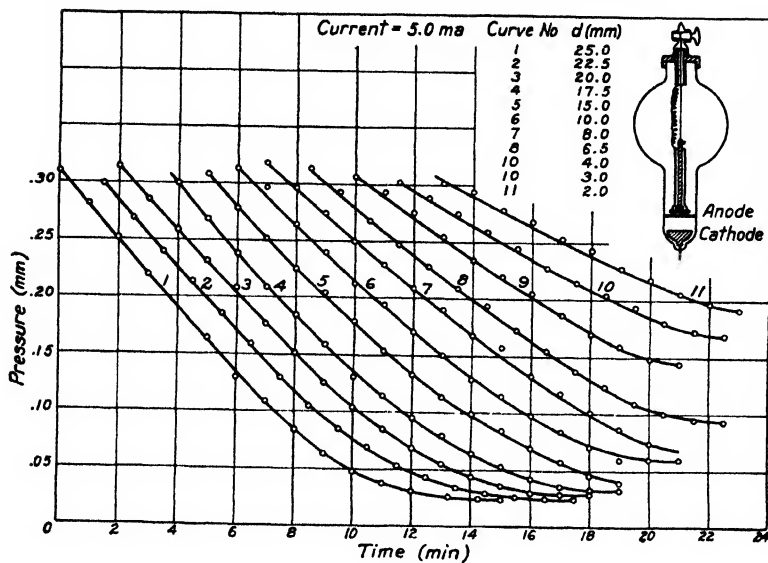


FIG. 1

Pressure vs. time curves for various electrode separations.

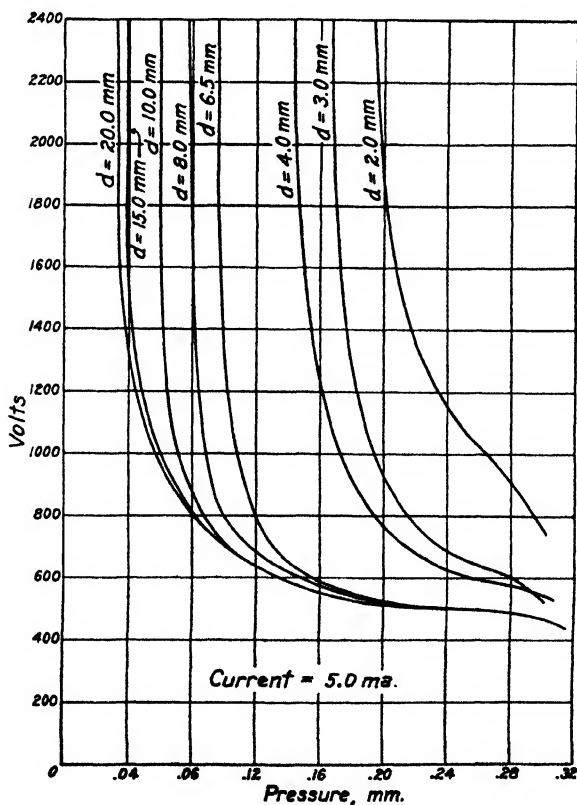


FIG. 2

Pressure vs. voltage curves for various electrode separations.

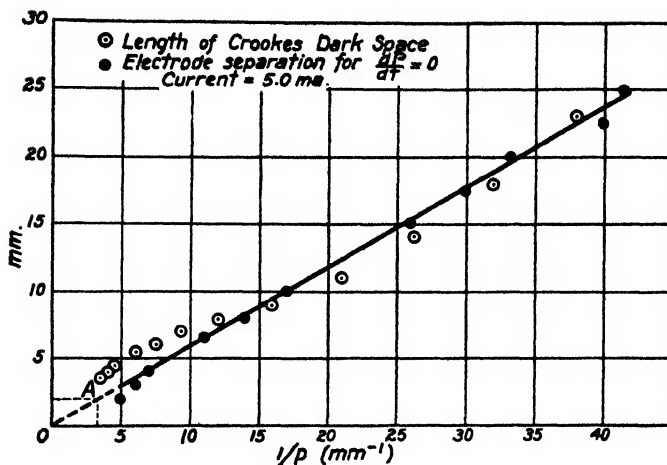


FIG. 3

Curve showing the relation between the length of the Crookes dark space and the electrode separation for zero rate as a function of pressure.

voltage necessary to maintain the current tended to cause the discharge to leak by the anode; the observed rates, therefore, are doubtless slightly high under these conditions.

The relationship between the Crookes dark space and the pressure at which the reaction ceases is shown in Fig. 3. The length of the Crookes dark space and the electrode separation at which the reaction becomes zero

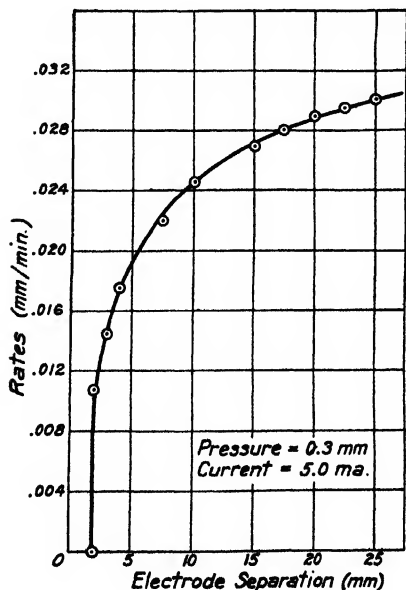


FIG. 4

Rate vs. electrode separation curve.

are plotted against the reciprocal of the pressure. It will be noted that the points fall close to the same straight line passing through the origin. The per cent error for short distances is necessarily higher than for greater distances; hence the observed deviations are not surprising. It should be mentioned that the dark space length was measured simply by visual observation; in another type of tube, designed for more accurate measurement, the hyperbolic relationship between length and pressure held accurately.

In Fig. 4 are plotted the rates measured at 0.3 mm. pressure for various electrode separations. The Crookes dark space at this pressure is very close to 2.0 mm. It will be observed that the rate decreases rapidly as the anode approaches the dark space.

The rate of decrease in reactivity per unit volume of negative glow in moving from the Crookes dark space to the Faraday dark space is shown in Fig. 5. When the log of the decrease in rate (maximum rate minus the observed rate) is plotted against the electrode separation the points fall on a straight line except where the anode is very close to the Crookes dark space. 0.030 was taken as the maximum rate, since it represented the rate

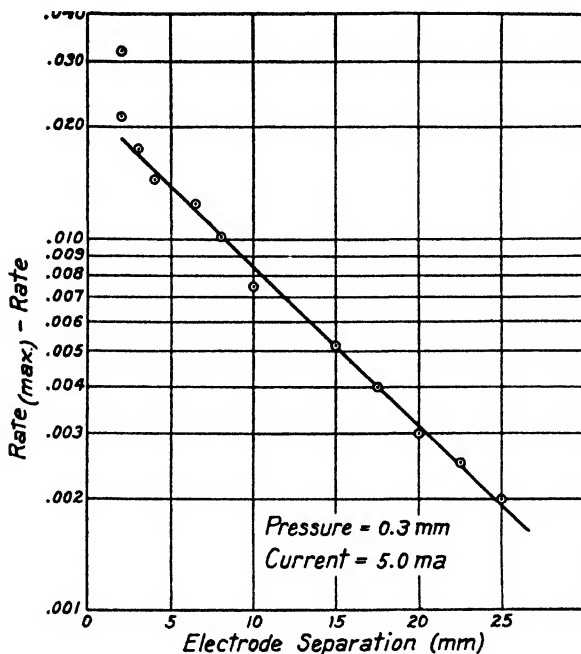


FIG. 5

Curve showing the rate of decay in reactivity through the negative glow.

observed when the entire negative glow was included between the electrodes. Thus it will be seen that the reactivity in the negative glow decreases exponentially with distance from the edge of the dark space.

Discussion of Results

Aston¹ has given the following expression for the Crookes dark space in the abnormal discharge,

$$d_a = \frac{A}{p} + \frac{B}{\sqrt{i}}$$

in which d_a is the length of the dark space in cm., p the pressure in mm. of mercury, i the current density, and A and B are constants. In the present experiments the current density was maintained constant so the relationship between length and pressure is expressed by

$$d_a = k_1/p + C$$

¹ F. W. Aston: Proc. Roy. Soc., **87**, 437 (1912).

From Fig. 3 it will be seen that the electrode separation at which $dp/dt = 0$ also obeys the relationship

$$l = k_2/p + C'$$

where l is the electrode separation. Since the points for both distances fall on the same line k_1 is equal to k_2 , and C and C' are equal and negligible at the low current densities used; hence $d_a = l$, i.e., the electrode separation at which the reactivity ceases is equal in length to the Crookes dark space. From this it follows that the reactivity in the dark space is negligible compared to that in the negative glow.

The mean path through which an electron is chemically active may be estimated from the rate of decrease of reactivity in the negative glow. Since the curve in Fig. 5 is exponential in character, except in the immediate neighborhood of the Crookes dark space, it follows from kinetic theory that for constant current and at a given pressure the decrease in the ability of an electron to induce reactivity can be expressed by

$$\frac{dp}{dt} = \int_{x=0}^{x=x} e^{-x/\lambda} dx$$

where x is the distance from the Crookes dark space, and λ is the mean path over which an electron is capable of inciting reaction. The value of λ obtained from the slope of the line is 2.5 mm. for 1 mm. pressure.

The fact that the exponential decay curve does not hold at the junction of the dark space may be due to several causes. When the anode is brought near the edge of the dark space the cathode fall of potential is not only materially raised, as is shown by Fig. 2, but the anode itself receives the direct impact of high-speed electrons. This bombardment gives rise to secondary electrons which produce an abnormal ionization in the gas adjacent to the anode. Another possible cause, inherent to the discharge itself, will be presented later on.

Interpretation of Results

The results that have just been presented can be interpreted readily from the physics of the discharge. In the discharge electrons are liberated from the cathode largely by metastable molecules and to some extent by positive ions and by photoelectric emission.¹ The electrons thus ejected are accelerated through the Crookes dark space by the cathode fall of potential. Very few positive ions are formed in the Crookes dark space since the length of the dark space is approximately equal to the mean free path of an electron between ionizing collisions. For instance, the dark spaces in nitrogen and oxygen at 1 mm. pressure are given by Townsend as 0.113 cm. and 0.114 cm., respectively. At this pressure the ionization mean free path of an electron is 0.113 cm. in nitrogen and 0.12 cm. in oxygen. These values as

¹ Note. Linder and Davis (J. Phys. Chem., 35, 3649 (1931)) postulate that the current passing through the discharge is carried to the cathode almost entirely by positive ions falling in from the dark space. This conclusion apparently grew out of a misconception of the length of the dark space and the mean free path of an electron between ionizing collisions. Direct experimental measurements of the number of positive ions arriving at the cathode (to be published shortly) shows the positive ion current to be less than 3% of the total current in N_2 at 1 mm. pressure.

obtained from kinetic theory are equal to $4\sqrt{2}$ times the molecular mean free paths times the probabilities of ionization upon collision. From this it follows that the average electron does not begin to ionize until it reaches the edge of the negative glow.

In spite of the fact that the edge of the dark space comes within a mean free path of the cathode a fraction of the electrons, as given by probability, will ionize in this region. The ions formed near the cathode give rise to the positive ion current received by the cathode; the ions formed near the outer edge of the dark space where the field is weak are apparently driven into the negative glow by the momentum of the electrons and thus give rise to the known increase in pressure of the gas at this point. It is these ions driven into the negative glow from the dark space that may in part be responsible for the high reactivity observed at the beginning of the glow.

It does not seem probable that the positive ions arriving at the cathode can contribute materially to the chemical action. The lowest pressure to which this reaction can be carried shows that an ion must make between 10 and 15 collisions with neutral molecules for reaction to take place. The mean free path of an ion in oxygen is 0.082 mm. at 1 mm. pressure. Such an ion, therefore, would make less than 14 collisions in traveling completely across the dark space. However, as was just pointed out, it is doubtless only the ions formed near the cathode that ever reach that electrode; hence the probability of making the required number of collisions with neutral molecules is relatively small. For this reason it is not surprising that Fig. 2 shows the distance from the cathode where the reactivity becomes zero is equal to the length of the dark space.

The number of positive ions formed per electron of current can be estimated from the exponential decay of reactivity in the negative glow. In making this estimation it is necessary to assume that the rate of reaction is proportional to the rate of positive ion formation; the M/N ratio is not involved.

The slope of the line in Fig. 5 gives the value $\lambda = 0.25$ cm. for the mean distance over which an electron is chemically active in the negative glow. Since the electron has already traveled through the Crookes dark space or 0.11 cm. before entering the negative glow the total path of the average electron at 1 mm. pressure is 0.36 cm. The mean free path of an electron times the probability of ionization, as has been stated, is equal to the length of the dark space of 0.11 cm.; hence the average number of ionizing collisions made by an electron is $0.36 \div 0.11 = 3.3$.

The total number of positive ions formed per electron under conditions quite similar to those found in the discharge can be estimated from an extrapolation of the results of Langmuir and Jones¹ or from the values given by G. A. Anslow,² both observers obtaining substantially the same results. Miss Anslow gives 3.7 positive ions for a 400 volt electron which is in reasonable agreement with 3.3 derived from the present data.

¹ Langmuir and Jones: *Phys. Rev.*, (2) 31, 357 (1928).

² G. A. Anslow: *Phys. Rev.*, (2) 25, 484 (1925).

These values assume that the energy of the electron is given by the entire cathode fall of potential. It may be, however, that the actual energy is slightly less than this, due to the space charge in the region through which the electrons are accelerated. In this connection it is interesting to note that Miss Anslow observed that an electron with 0.36 cm. range at 1 mm. pressure produced 3.4 ions, the required accelerating voltage being 347. Since 3.3 ions are obtained for a 0.36 cm. range in the present experiments, it might be inferred that the electrons in passing through the Crookes dark space failed by about 50 volts of receiving an acceleration corresponding to the entire cathode fall of potential.

The value of the M/N ratio can now be placed within reasonably narrow limits. The time vs. pressure curves for 2.5 cm. electrode separation indicate a yield at 0.3 mm. pressure of 1.5 molecules of NO_2 synthesized per electron of current. In the first paper on oxidation of nitrogen it was shown that this reaction is initiated by N^+_{2} ions, O^+_{2} ions being relatively inert. Since the stopping powers of oxygen and nitrogen are very nearly identical, the ratio of N^+_{2} to O^+_{2} ions is as 1:2. This gives an equivalent yield of 1.5 molecules formed per 1.1 N^+_{2} ions, assuming positive ion current to be negligible. The positive ion current at 0.3 mm., however, has been found by direct measurement to be 15% of the total current; thus the number of electrons producing ions is reduced by 15%, and further the number of ions formed suffers an effective loss corresponding to 15% of the entire current since the positive ions arriving at the cathode do not contribute materially to the synthesis. Making these corrections the number of N^+_{2} ions available for reaction is 0.73 per electron of current. The value of M/N , therefore, is $1.5/0.73 = 2$, approximately.

Summary

The chemical action taking place in the Crookes dark space and the negative glow of the ordinary glow discharge has been measured for the synthesis of nitrogen dioxide. The distance from the cathode within which no appreciable reactivity occurs is shown to be equal to the length of the Crookes dark space. The reactivity per unit volume of discharge is a maximum at the beginning of the negative glow and thereafter decreases exponentially through the glow.

The average path at 1 mm. pressure over which electrons ejected from the cathode are capable of inciting reaction is shown to be 0.36 cm., the reactivity being confined entirely to the last 0.25 cm. of path. The total number of positive ions formed per electron is given by dividing 0.36 cm. by the mean free path of an electron between ionizing collisions. Thus the measurement of the mean free path over which the electrons are chemically active enables the number of positive ions formed in the negative glow to be computed by a new and independent method. The value of 3.3 ions so obtained agrees fairly well with 3.7 reported by Miss Anslow for 400 volt electrons.

The ratio of $M/N = 2$ for N^+_{2} ions is obtained by correcting for the loss of N^+_{2} ions to the positive ion current.

ELECTROKINETIC PHENOMENA

VIII. Surface Conductance of Cellulose and the Theory of Smoluchowski*

BY HAROLD A. ABRAMSON

In a recent series of papers dealing with the properties of the cellulose-water interface, Briggs¹ and Bull and Gortner² have described excellent methods for the measurement of surface conductance. They have, in addition, published most extensive and interesting reports of the effect of electrolytes on the specific surface conductance, $(\kappa_s - \kappa)$, of cellulose diaphragms. Briggs pointed out that electrolytes produced, in general, a continuous *increase* in the surface conductance but a *decrease* in the ζ -potential after a primary small increase. This was apparently completely contrary to the predictions of Smoluchowski³ who postulated a concurrent increase of $(\kappa_s - \kappa)$ and ζ . It is the purpose of this communication to reconsider certain data of the authors mentioned above in the light of Smoluchowski's theory and that of Gouy⁴ and of Debye and Hückel.⁵ It will be shown that the general changes of $(\kappa_s - \kappa)$ and ζ are not inconsistent with the theory of Smoluchowski if the thickness of the double layer is considered, but that the theory is incomplete.

Theoretical

Consider with Smoluchowski³ a cylindrical glass capillary having the property of surface conduction where the radius of the capillary is large compared with, d , the thickness of the double layer. The ratio of the current carried by the surface phase to that of the bulk is,

$$\frac{I_s}{I} = \frac{S}{Q\eta\kappa d} \left(\frac{\zeta D}{4\pi} \right)^2$$

where $\zeta \propto \frac{E}{P} (\kappa_s)$; S = circumference of capillary; D = dielectric constant;

Q = cross-section; η = coefficient of viscosity of the liquid; κ = specific conductance of the liquid in bulk; E = streaming potential; P = the pressure difference; κ_s = specific conductance of the liquid in the capillary; units are c.g.s. electrostatic. Briggs developed a method for determining the specific conductance of the bulk liquid in cellulose diaphragms so that he could replace I_s/I by its equivalent $(\kappa_s - \kappa)/\kappa$, yielding

$$\kappa_s - \kappa = \frac{S}{Q\eta d} \left(\frac{\zeta D}{4\pi} \right)^2 \quad (1)$$

In order to compare $(\kappa_s - \kappa)$ and ζ when the concentration of electrolyte is changed, it is necessary to sort out the constants. In a given cellulose dia-

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phragm with small changes in concentration of salt $[S/Q\eta (D/4\pi)^2]$ can be taken as approximately constant, but ζ and d are variables.

The theory of Smoluchowski as here considered postulates that

$$(\kappa_s - \kappa) = C (\zeta^2/d). \quad (1a)$$

$C = \text{a constant.}$

The specific surface conductance should increase not simply with ζ , but rather with the ratio (ζ^2/d) . It is possible to calculate values of d in different salt solutions by the theories of Gouy and of Debye and Hückel. Both of these give essentially the same results. We employ the relationship of Debye and Hückel.

$$d = \frac{1}{\Gamma} = \frac{3.06 \times 10^{-8} \text{cm.}}{\sqrt{\mu}} \quad (2)$$

where as usual the ionic strength, $\mu = \frac{1}{2} \sum_i n_i Z_i^2$, n = number of ions of the valence Z . Combining equations (1) and (2),

$$(\kappa_s - \kappa) = C(\zeta^2\Gamma) \quad (3)$$

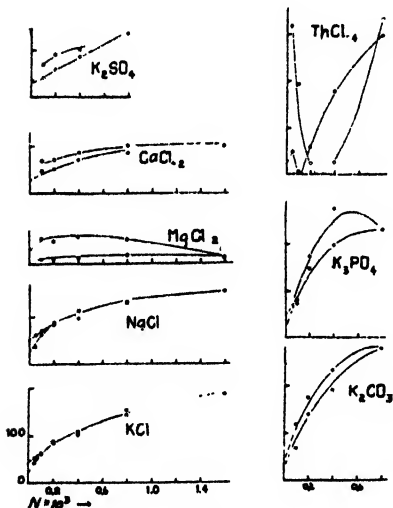


FIG. 1

Both $(\zeta^2\Gamma)$, closed circles, and $(\kappa_s - \kappa)$, open circles, increase as the salt concentration is increased, although the simple theory of Smoluchowski is evidently not followed. Data of Bull and Gortner.

The ionic strength of the distilled water cannot be neglected because very dilute salt solutions are to be considered. A minimum value of μ was obtained by extrapolating $([E/P \kappa_s]^2\Gamma)$ to zero salt concentration considering the ionic strength as due to the salts alone. This extrapolation yielded $\mu = 25 \times 10^{-6}$.

Relationship of $(\kappa_s - \kappa)$ and $(\zeta^2\Gamma)$. To test equation (3) we have evaluated from the data of Bull and Gortner values of $(\zeta^2\Gamma)$ in different concentration of various salts for the cellulose-water interface. These values have been plotted as ordinates as closed circles in Fig. 1, against the concentration of electrolytes. On the same ordinate by converting the highest value of $(\kappa_s - \kappa)$ to the same scale $(\kappa_s - \kappa)$ has been also plotted. In every instance, for KCl, NaCl, MgCl₂, CaCl₂, K₂SO₄, K₂CO₃, K₃PO₄, ThCl₄, there is a general

parallelism between $(\kappa_s - \kappa)$ and $(\zeta^2\Gamma)$, with, however, differences given by the areas and their shapes between the two sets of data which indicate that although the combined Smoluchowski and Debye theories as employed here give a qualitative expression of agreement it is evident definite differences exist between theory and experiment. This is brought out perhaps more clearly in Fig. 2, where $(\zeta^2\Gamma)$ has been plotted directly against $(\kappa_s - \kappa)$ for

LiCl, NaCl, KCl, CsCl, NH_4Cl and HCl (Briggs). The small black rectangle in the lower left-hand corner is the mean for values of $(\zeta^2\Gamma)$ in distilled water. The ordinate value of this rectangle is probably too low because of the low and uncertain value of μ for the distilled water. The dotted paraboloid curves starting at this rectangle fit the data fairly well. However, according to equation (3) when $(\kappa_s - \kappa) = 0$, $(\zeta^2\Gamma)$ should also be zero. If the theory were followed in an ideal case, the data should have extrapolated through the

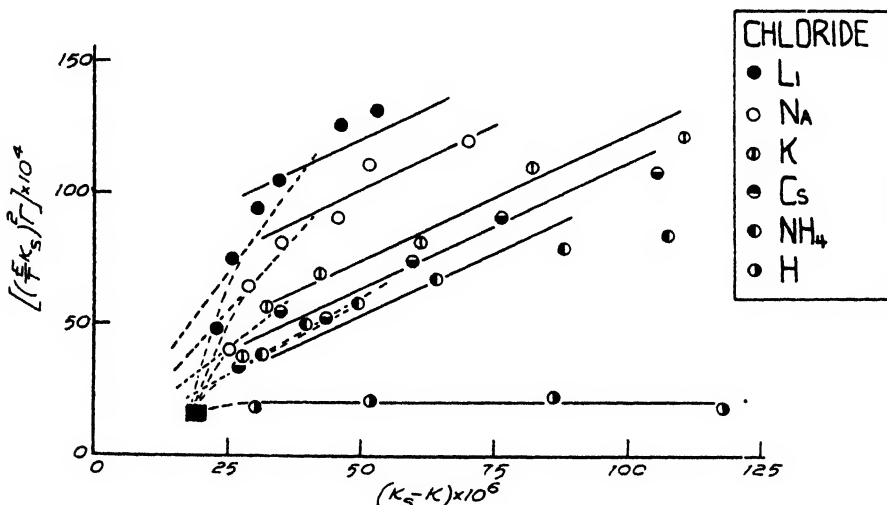


FIG. 2

origin as indicated by the broken straight lines. It must be remembered that the ions present in distilled water are different from those of each of the added salts. Since we are obviously dealing with changes due to the specific nature of the ions it is not logical to expect the simple theory to hold and the extrapolation through the origin to occur. The straight unbroken lines drawn through the data fit the latter portions of the curve poorly, the paraboloid plot being a closer fit. A clue which may lead to the correct theory has been given by Briggs who pointed out that $(\kappa_s - \kappa)$ for a given value of κ followed very closely the mobilities of the alkali halides. That is, the specific surface conductance was found to be simply related to the mobility of the cation alone. This is made clearly evident in Table I where values of (κ) and $(\kappa_s - \kappa)$ obtained from Briggs and Bull and Gortner are compared for a series of salts. If the surface conductance were to vary with the mobility of the cation, then for a given value of κ the ratios $\frac{\kappa_s - \kappa}{\text{mobility cation}}$ should be constant.

This result is obtained for Li^+ , Na^+ and K^+ but not for Mg^{++} and Ba^{++} . In the simple case of the alkali halides it would seem logical to expect a modification of the theory calling for a relationship of the sort given by Mooney⁶ who considers the surface conductance as partially dependent upon the absolute mobilities of the positive and negative ions.

Professor R. A. Gortner has been kind enough to read and check parts of the calculations.

In Table I for various values of κ , the surface conductance ($\kappa_s - \kappa$) is compared with the mobility of the cation for a series of salts. If the surface conductance follows the order of the mobilities of the cations with the same anion then for any given value of κ the ratios $\frac{\kappa_s - \kappa}{V_{\text{cation}}}$ should be constant. Note the excellent agreement with this assumption for lithium, sodium and potassium chlorides. It does not hold for divalent cations and those of higher valence. The values of ($\kappa_s - \kappa$) are taken from smooth curves drawn from data of Briggs and Bull and Gortner.

TABLE I

κ $\times 10^5$ mhos	LiCl		NaCl		KCl		MgCl ₂		BaCl ₂	
	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s - \kappa}{V_{\text{Li}^+(33.3)}}$	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s - \kappa}{V_{\text{Na}^+(43.4)}}$	$\kappa_s - \kappa$ $\times 10^5$ mhos	$\frac{\kappa_s - \kappa}{V_{\text{K}^+(64.5)}}$	$\kappa_s - \kappa$ $\frac{2(\kappa_s - \kappa)}{V_{\text{Mg}^{++}(45.9)}}$		$\kappa_s - \kappa$ $\frac{2(\kappa_s - \kappa)}{V_{\text{Ba}^{++}(55.4)}}$	
5	38	115	44	103	56	87	33	72	41	74
10	46	139	58	134	82	127	37	81	50	90
15	51	155	66	152	98	152	39	85	56	101
20	56	170	70	161	107	166	40	87	60	108
(40)	(60)	(182)	(82)	(189)	(122)	(189)	(40)	(87)	(68)	(123)

Professor K. S. Cole has been kind enough to discuss certain aspects of this problem with me.

Summary

It is shown that certain data on the effects of salts on the surface conductance of cellulose are not inconsistent with the combined theories of Smoluchowski and Debye and Hückel, but that the data indicate the incomplete form of the classical theory.

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THE SOLUBILITY OF GOLD IN MERCURY. V*

BY JOSEPH T. ANDERSON

The object of the present investigation was to supplement the determinations of the solubility of gold in mercury already made in this laboratory^{1,2,3,4} by advancing to higher temperatures. The range covered was from 280° to 400°C, a region concerning which existing evidence is rather discordant. For the most part the synthetic method was used.

The determination of solubility by the synthetic method consists in sealing up in a glass tube the system of which the solubility (liquidus) point is desired and, by properly heating, determining the temperature at which the last crystal of solid disappears. As used for non-metallic systems between 10° and 80°C the tubes are heated in a water bath with constant stirring and shaking, and if fine crystals are used and the heating is very slow over the last temperature range, the temperature at which the last crystal disappears can be determined with considerable accuracy.

To adapt this method to the higher temperature range it was necessary to find a substance for the bath which would be transparent fluid without objectionable properties at temperatures up to 400°C. The simplest kind of bath which can be used is an air bath. There are however disadvantages in the use of air due to its low specific heat and poor thermal conductivity, both of which tend to allow temperature differences to exist in the bath. After considerable casting about, no satisfactory liquid had been found and it was decided to use an electrically heated air bath.

Description of Furnace

The furnace used by Weiner³ was redesigned as follows with the objects in view of improving the temperature uniformity and making it possible to see into the furnace readily in order to observe the disappearance of the solid. The four 500 watt nichrome elements which were in each of four corners of the furnace were replaced by B. and S. No. 30 Ni wire elements of which there were ten in parallel, wound side by side on four transit strips so that each of the elements went completely around the inside of the furnace eight times. This made the inside of the furnace surrounded on four sides (not the ends) by wires spaced about 3/16" apart, each tenth wire being part of the same element. Each of the elements developed about 250 watts on 110 volts a.c. They were connected so that two sets of two each could be put either in series or in parallel and a 50 ohm rheostat was provided which could be put in series with either or both of two elements. It was found possible to regulate the heat input to any desired value by these means.

* Communication from the Chemical Laboratory of the University of Rochester, Rochester, N. Y.

After reaching the required temperature, it was never found necessary to use more than 1000 watts to maintain that temperature. In order to make it possible to get into the furnace without going through the heating elements one end of the furnace was made detachable. This end was provided with a 2" \times 3" plate glass window.

Since there were found to be differences in temperature within the bath amounting to ten degrees it was necessary to stir the air. This was first done by large sheet metal vanes mounted on the shaft which rocked back and forth to stir the contents of the solubility tubes which were attached to it. More vigorous stirring was obtained by a large bent piece of sheet metal attached to a separate shaft which entered through a hole in the window and was rotated in such a way as to make the air move toward the center of the furnace as well as rotate. Later the stirring was done by an ordinary 6" air fan which also was attached to the shaft which entered through a hole in the window. With either of the two last mentioned fans there was probably not more than about a degree difference in temperature in the parts of the bath in which the tubes were.

Measurement of Temperature

The mercury thermometers used were of good grade, made by Taylor Instrument Company and by Hiergesell Brothers (see Table II) and were graduated in one-degree divisions. The bulb of the thermometer used was immersed in molten metal contained in an ordinary iron crucible. In order to eliminate stem correction and still allow it to be read, the thermometer was placed inside a heated chimney of pyrex glass which kept the mercury column at the same temperature as the bulb. The chimney was constructed as follows: Small glass drops were sealed every centimeter for 20 cm. on two opposite sides of the outside of a pyrex tube 5 cm. in external diameter. Nichrome ribbon, 4.1 ohms per foot, was then wound tightly on the tube so that the glass drops separated the windings. A large pyrex tube, 6 cm. internal diameter and long enough to cover the winding, was placed over the first leaving 6 cm. of the smaller tube projecting and the space between the tubes was closed at each end by asbestos which was moistened and forced into place. The portion of the smaller tube protruding fitted into a hole in the top of the furnace and this supported the chimney.

By means of a 50 ohm rheostat in series on 110 volts a.c. the temperature of the chimney could be kept at any temperature used in the furnace. The temperature of the chimney was read by an auxiliary thermometer the bulb of which was placed about half way up the chimney. Although the temperature of the chimney varied considerably from top to bottom, it seems very probable that by its use the stem correction for the main thermometer was reduced to less than 0.1°.

The thermometers used were standardized by comparing with a Hiergesell Brothers double-diamond 360° thermometer which was graduated in 1/2 degrees and had been standardized by the Bureau of Standards. The thermometers were standardized under the same conditions as those under

which they were used, employing the fused metal bath and the chimney. The readings of the thermometers were taken every ten degrees from 280° to 360°C. At each point the temperature was held constant to within 0.2° for twenty minutes and readings were made to the nearest 0.1° using a small magnifying glass. Ice points were taken at the time of standardization and were checked frequently throughout the runs.

With continued use at temperatures over 300° the ice points of the thermometers were found to change in some cases as much as a degree. In order to eliminate the uncertainty thus introduced it was decided at about the midpoint of the investigation to change to a platinum resistance thermometer. The thermometer obtained was of the best grade made by Leeds and Northrup, having a resistance of 2.5 ohms cold. The bridge was of the semi-precision type being graduated to 0.01 ohms which corresponds to one degree and readable to 0.1°. The galvanometer was of the mirror type, having a self-contained light and ground-glass scale and was found to give a deflection of about 3 divisions per 0.1° thus making it possible to notice and correct very slight changes in temperature. Correcting small changes in temperature was further facilitated by the fact that, with the heating elements located as they were inside the furnace, the lag between the time when the current was increased and when the temperature started to rise was only 10 or 15 seconds.

The resistance thermometer was calibrated^{13,14,15} at the ice point, steam point, and sulfur boiling point. During constant use over a period of about ten weeks the resistance of the thermometer at zero increased 0.009 ohms or the temperature for a given resistance fell 1.0°, the change being practically the same at all temperatures. Four calibrations were made and for the first, third, and fourth the changes were found to be fairly uniform as contrasted with the haphazard changes in the zero points of the mercury thermometers. The results of the second calibration were discordant with the others and therefore it was considered that there was a mistake in the calibration.

It has been found that the resistance (R) of platinum can be expressed to a high degree of accuracy as a parabolic function of temperature (t). The equation used is

$$R = R_0 + at + bt^2$$

in which the three constants R_0 , a , and b are evaluated by determining R at the temperatures of melting ice, boiling water, and boiling sulfur. The change of boiling point with barometric pressure has to be taken into consideration and at the sulfur boiling point other factors also including radiation, condensation of vapor, and lagging of the vapor chamber. The methods have been standardized by the Bureau of Standards and are specified in the papers referred to above. The values of resistance found at zero and at the normal boiling point of water and sulfur in the four calibrations are given in Table I, along with the values for the constants in the resistance-temperature equation.

TABLE I

Constants* for L. & N. Resistance Thermometer No. 184209 for the equation $R = R_0 + at + bt^2$

Calibration	R_0	$R_{100.00}$	a	$R_{444.60}$	b
1st	2.471	3.441	.009846	6.556	-.000001483
(2nd	2.473	3.437	.00977	6.558	-.00000132)
3rd	2.479	3.448	.009835	6.563	-.000001457
4th	2.480	3.450	.009850	6.565	-.000001488

* Using semi-precision bridge No. 207751 and galvanometer No. 219054.

In using the resistance thermometer in the furnace the metal bath and the heated chimney were done away with, the coil of the thermometer being placed as near as possible to the solubility tubes and at the level at which the amalgams were most of the time, namely about one inch below the center shaft.

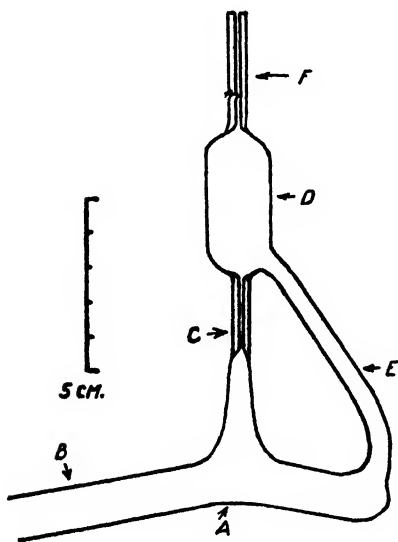


FIG. 1

Synthetic Tube. The capillary really has no constriction.

Solubility Tubes

Since liquid amalgams are not transparent it is not possible to observe the disappearance of crystals simply by looking at the tube as is done with ordinary systems. Accordingly a tube was designed as shown in Fig. 1 made of pyrex glass tubing with a fine capillary C of the same bore as that previously used in solubility tubes in this laboratory, and a return tube E. The amalgam of desired composition is introduced into A and the tube is sealed off at B. The whole tube is evacuated to a few thousandths of a millimeter of mercury through the coarse capillary F and this is then sealed off near the bulb D. When the tube is turned counter clockwise 180 degrees the contents fall onto the capillary C and the liquid filters through, leaving the solid behind. When

the tube is further rotated in the same direction (counter clockwise) the liquid runs back through the tube E into A. By continuously raising the temperature, filtering at frequent intervals, the amount of solid is observed to decrease and the temperature at which no more solid is found is the solubility temperature provided the rate of heating is slow enough and other conditions are such that the system is in equilibrium. In some of the later runs tubes were used which had about the same overall dimensions as that shown in Fig. 1 but only about half the volume since smaller tubing was used in making them. No difference in results was attributed to this change.

The tubes were supported by a shaft which was in the center of the furnace. Each tube was fastened to the shaft by two clamps, one of which

held it about part A and one about part D. Two tubes could be run at the same time by placing the capillaries (C) of the two on opposite sides of the shaft so that the solid which filtered out could be seen in both. The shaft rocked back and forth so that the contents of the tube were transferred from one end of part A to the other about twenty times per minute. To furnish light a 50 watt show case bulb was partially inserted into the furnace through a hole in the end opposite to the window.

Synthetic Runs

The mercury used in the first part of the runs was the same used by Weiner³ and that used later was purified by Mr. DeRight. Both lots were triple distilled in sealed glass systems. The gold used came from the United States Assay Office and was said to be at least 999.8 fine. In some of the runs gold was used which had been recovered from earlier runs by vaporizing the mercury at temperatures up to 550°C in a current of air. Knowns treated in this way show that the mercury is completely removed.

The tubes were evacuated in order to prevent oxidation of the mercury and also incidentally to keep down the total pressure in the tubes at high temperatures. Oxidation is objectionable not only because of the mercury removed but also because the solid oxide may interfere with the filtering, or may be mistaken for crystals of the solid phase, or may stick to the walls of the tube and hold with it crystals of solid. It is also very possible that the presence of the oxide may give a ternary system which has a solubility point different from that of the simple system gold-mercury. The pressure existing inside the tubes when cold was from 0.001 to 0.005 mm. of mercury as measured by a McLeod gauge.

In making a synthetic run the temperature of the furnace was raised rather rapidly, slowing down the rate of heating as the amount of solid left decreased, and the temperature of complete disappearance was determined within a degree or two with comparative ease. To obtain crystals again the furnace was cooled, the temperature of reappearance being generally two or three degrees lower than the temperature of disappearance. The temperature was then increased slowly and the solubility point determined.

The rate of heating at the solubility point was restricted by the fact that filtrations could not be repeated much more frequently than at two minute intervals. Since it was desired to determine the solubility point to the nearest tenth of a degree the average rate of heating at the solubility point could not be greater than 0.1° in 2 minutes or 1° in 20 minutes. Often the solubility temperature was approached much more slowly than this.

Tubes numbered up to XXXIV were made up and run according to this procedure and the results are shown in Table II and in Fig. 4 together with other data which will be described presently. In the case of tubes VI, IX, and X after the solubility point had been determined the tube was opened, a weighed amount of gold was added, and the tube was evacuated and sealed up and used as a new tube. The tubes so prepared were numbered VI-I, IX-I, and X-I respectively. It was finally decided to be better practice to start with fresh materials each time.

TABLE II

Results of Synthetic Runs

Tube No.	Gms. Au	Gms. Hg	At. % Au	Temp. °C	Thermometer	Remarks
II	3.875	34.647	10.22	286.3	T-1	one run, tube cracked and contents were transferred.
IV	5.444	36.502	13.17	288.2	"	several runs.
V	4.788	32.121	13.17	291.1	"	one run.
VI	4.771	31.927	13.19	290.8	"	one run.
VI-I	5.312	31.927	14.48	293.5	"	one run.
VII	5.264	31.551	14.51	293.9	"	one run, disappearance and reappearance.
VIII	5.152	30.915	14.50	293.9	"	do.
IX	5.678	30.174	16.07	297.9	H	one run.
IX-I	6.085	30.174	17.02	300.4	"	one run, $\pm 1/2^\circ$
X	6.272	31.135	17.01	300.7	"	one run.
X-I	7.838	31.135	20.40	307.2	"	3 runs, 2 checks.
XII	6.026	20.592	22.94	310.2	"	one run, possibly low.
XIII	5.767	19.888	22.78	309.4	"	2 runs, rather scanty, possibly low.
XIV	7.143	21.716	25.07	315.2	"	one run.
XVI	7.459	20.454	27.05	320.7	T-2	one run.
XVII	8.447	21.015	29.02	327.5	"	one run.
XVIII	8.746	21.740	29.04	328.6	"	one run.
XIX	9.493	21.503	31.00	334.5	"	2 runs, $1/2^\circ$ difference.
XXII	6.709	21.640	23.97	315.4	"	2 runs, possible high, impurity suspected.
XXIV	7.251	19.978	26.97	321.7	"	one run, impurity suspected.
XXV	9.872	19.272	34.26	351.0	Pt(1,3)	one run.
XXVI	9.724	18.980	34.26	352.6	"	one run.
XXVII	11.824	19.659	37.96	373.4	"	one run.
						2 disappearances.
XXVIII	12.252	20.368	37.96	374.8	"	do.
X-I		see above		308.9	"	one run.
XVII		see above		327.5	"	one run.
XIX		see above		335.9	"	one run.
XXIX	4.456	6.728	40.25	388.8	Pt(3)	5 runs varying over 3° , highest value given.
XXX	8.825	13.500	39.94	386.8	"	4 runs varying over 1° , highest value given.
XXXI	3.200	19.983	14.01	298.7	"	4 runs varying over 5° , highest value given.
XXXIII	1.986	14.139	12.50	286.5	"	2 runs, 4° difference, higher value given.

TABLE II (Continued)

Results of Synthetic Runs

Tube No.	Gms. Au	Gms. Hg	At. % Au	Temp. °C	Thermometer	Remarks
XXXIV	2.009	14.237	12.55	288.3	Pt(3)	2 runs, 4° difference, higher value given.
XVII		see above		329.6	"	one run.
XIX		see above		337.7	"	one run.
XVII		see above		326.7*	Pt(4)	one run, (two disappearances).
XIX		see above		331.8*	"	do.
X-I		see above		308.6	"	do.
XXVIII		see above		368.3	"	do.
XXXI		see above		296.9	"	one run.
XXXII	4.055	17.570	19.01	307.2	"	4 runs varying over 3°.
XXXV	2.910	15.548	15.99	300.2	"	2 runs, 1/2° difference, higher value given.
XXXVI	4.891	13.493	26.94	322.5	"	2 runs, 2° difference, higher value given.

Thermometers

T-1; Taylor 7A297924, nitrogen-filled mercury thermometer.

H; Hiergesell Bros. 3389, nitrogen-filled mercury thermometer.

T-2; Taylor 7A553812, nitrogen-filled mercury thermometer.

Pt (1,3); platinum resistance thermometer, average of the first and third calibrations.

Pt (3); platinum resistance thermometer, third calibration.

Pt (4); redesigned furnace; platinum resistance thermometer, fourth calibration; average of reading in holes J and K.

* These runs were made before the window was lagged with magnesia. A correction which was found for tube X-I by running it before and after installing the magnesia was applied to the results found to give the temperatures listed.

Analytical Runs—General Method

There is a great diversity of opinion among those who have worked on the system gold-mercury as to what compounds are formed. Therefore, in order to throw light on the nature of the crystals that separate from a saturated solution of gold in mercury, it was decided to attempt to determine the composition of the solid phase in equilibrium with the saturated solution at a few temperatures in the region of this investigation.

The tube used is shown in Fig. 2. Mercury and an amount of gold more than enough to saturate the mercury at the temperature to be used were sealed in part A and the tube was evacuated through D and sealed off as the other tubes were. The tube was fastened to the shaft by means of clamps around part A and part C in such a manner that the shaft was just below part A of the tube in the position shown in Fig. 2. The tube was then rocked back and forth, over a large enough angle to transfer the materials from one end of A to the other, for a long time at the required temperature. When it was certain that the system had attained equilibrium the tube was inverted by turning the shaft 180 degrees, causing the contents of the tube to fall on

the porous glass disc¹⁶ B. The shaft was then quickly started revolving at about 2000 r.p.m. and the centrifugal force held the solid amalgam against the glass disc, forcing the liquid through the disc into part C of the tube. After whirling for one or two minutes the tube was cooled and the crystals left on the glass disc were removed, put in a weighed crucible, and analyzed by evaporating the mercury and reweighing. The part of the amalgam which had gone through the filter was also analyzed, since this gave a value for the

solubility of gold in mercury as well as a check on whether any of the materials put into the tubes had been lost in removing from the tube or in analyzing.

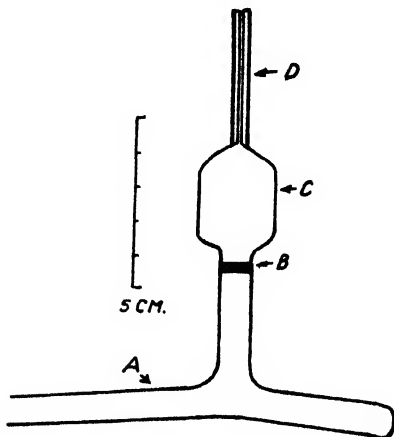


FIG. 2
Analytical Tube.

Description of the Redesigned Furnace

Since the furnace used in the synthetic runs did not have as good temperature uniformity as might be desired (there were variations of about a degree in the region of the tubes) it was redesigned to allow the tubes to be whirled, an effort being made at the same time to improve the uniformity. The rebuilt furnace is shown in Fig. 3. All the heating elements were removed from inside the copper shell A and six new nichrome ribbon

elements were wound around the outside of the electrobestos which covered the copper. The elements were wound side by side as before but each one went around the furnace only five times. The ribbon had a resistance of about 2 ohms per foot and each element was about 19 feet long and developed about 320 watts on 120 volts a.c. Outside of the heating elements were a $1\frac{1}{2}$ " layer of super-x and a $1\frac{1}{2}$ " layer of 85% magnesia. Outside of all was a shell of galvanized sheet iron which held the magnesia and super-x in place. Following the design of Kracek¹⁹ the fan was mounted on a tubular shaft and a second smaller shaft entered the furnace through the hole in the tube. The shaft B of 1" brass tubing was supported outside the furnace by two Smith self-aligning bearings entered through a hole in the left end. The shaft carried an 8" air fan C and was driven by an electric motor at about 3000 r.p.m. Through the brass tube was inserted a longer shaft D, $\frac{5}{8}$ " in diameter, which was supported outside the furnace by two Smith self-aligning bearings and inside by a third E. To this shaft the tubes were fastened by means of the clamps F and G. The shaft could either be rocked back and forth to stir the contents of the tubes or whirled to make the liquid filter through the porous glass discs. The counterweight H was adjusted so as to prevent excessive vibration when the tubes were being revolved. With the tubes held in the clamps as described the radius from the center of the shaft to the glass disc was about 4 cm. This distance was limited by the size of the furnace. When making synthetic runs the counterweight was removed and the collar

holding the clamps G was put in its place. This brought the center of the tubes (Fig. 1) near the shaft and therefore kept the tubes always near the center of the furnace when they were being turned around to filter off the liquid. Keeping the tubes in one part of the furnace is essential to obtain uniformity of temperature as they are rotated. That this condition was not fulfilled and therefore the temperature may have varied in the analytical runs during whirling is not considered important since the precision of the analytical runs is considerably lower than that of the synthetic runs.

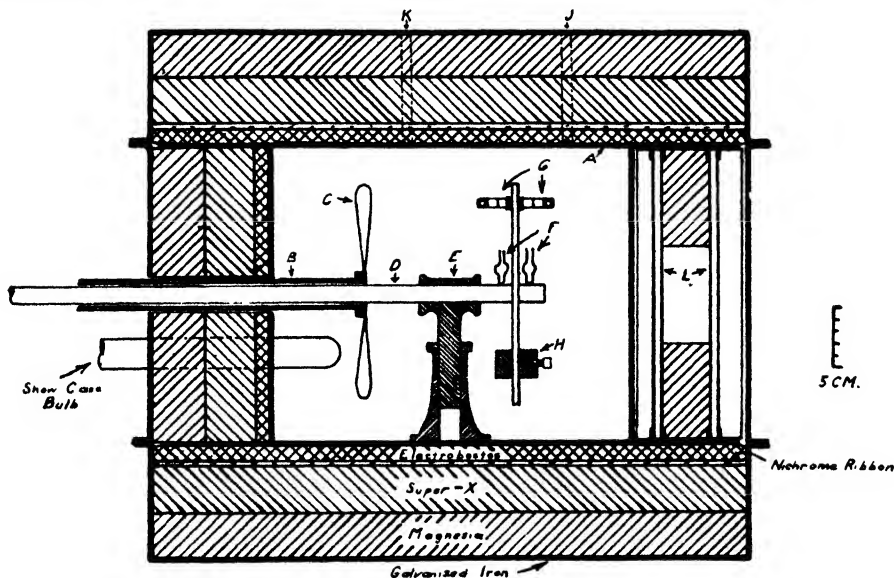


FIG. 3

The resistance thermometer was placed in either hole J or K and the sensitive coil of the thermometer was placed at the same level as that at which the amalgams were when the tubes were being rocked. The temperature recorded was generally an average of the temperatures indicated in the two holes since the tube was between them and the chief cause of temperature variation in the direction of the shaft was considered to be the loss of heat through the double plate glass window L. After use for some time this loss was cut down by filling the space between the glasses with magnesia except for a $3\frac{1}{2}$ " hole in the center. The difference in temperature between points of equal level below holes J and K seemed to change also with the speed of the fan. For a number of runs the difference was found to be 2° . Vigorous stirring helps to correct differences in temperature but also may aggravate the condition by sucking in cold air if the rate of stirring is high enough and there are any cracks in the furnace walls. All the holes behind the fan were filled with furnace cement but the indication was that air entered in some way at least when the speed of the fan was great. With the thermometer in the same hole, the variation of temperature with height seemed to indicate that the center was the coolest part of the furnace and that the temperature

increased toward the walls. Within the region occupied by the tubes the variation of temperature was probably not one degree. It had been hoped to obtain better uniformity than was found. It would appear that for much better uniformity than that obtained, a bath of some fluid other than air would have to be used.

Procedure in Analytical Runs with Gold and Mercury alone

In some of the analytical runs the equilibrium temperature was approached from the high side and in some from the low side. The temperature of the furnace was held at least within about 10° of the final temperature for from three hours to eight hours and usually it was held within 0.1° for an hour or more before the solid and liquid were separated by whirling. As the tubes cooled after filtering some mercury condensed on the inside of the outer walls in the parts of the tube on both sides of the glass disc. The amount condensed seemed more than the amount of mercury which would be expected to be in the vapor form in the tube and it was feared that the mercury might have vaporized from the mercury rich portion below the disc (part C Fig. 2) and passed through the disc to condense on the walls of part A and also on the solid crystals and so have changed the composition of the solid. In one run the bottoms of the tubes (parts C) were quickly cooled with water after whirling to prevent vaporization of mercury from that part of the tube and in other runs a coarse capillary was included in the tube between the porous disc and part C and this capillary was sealed off as soon as possible after the whirling. Since these procedures did not apparently change the amount of condensed mercury in part A, the mercury condensed on the outer walls of part A must either have been present in that part as vapor or have come from the solid phase, distilling to the walls, because they cooled first. Apparently, therefore, no error was introduced by mercury vapor passing through the porous glass disc during cooling.

The analysis of the gold-mercury mixtures was accomplished by heating them in porcelain or sillimanite crucibles in a current of air, thereby vaporizing the mercury. The greater portion was vaporized slowly at or below $300^{\circ}\text{C}.$ to avoid spattering, and the temperature was then raised to about 500° to remove all but the last traces of the mercury. The last traces were then driven off by heating the crucibles with an oxygen-gas flame rather poor in oxygen, until the gold was just melted. The crucibles were then cooled in a desiccator and weighed. These weights, together with the weights before heating and the weights of the empty crucibles, give the compositions of the samples.

The contents of tubes XXIX and XXX were analyzed by this method and the resulting amounts of gold and mercury found checked the amounts put into the tube to within $1/5$ of a part per thousand for both tubes. The results indicate that the method of analysis is more than accurate enough for the purpose. The weights taken and found are given in Table III.

TABLE III
Analysis of Knowns for Gold and Mercury

		Taken	Found	Error
XXIX	g.Au	4.4557	4.4560	high 0.3 mg.
	g.Hg	6.7276	6.7288	high 1.2 mg.
XXX	g.Au	8.8249	8.8161	high 1.2 mg.
	g.Hg	13.4995	13.4968	low 2.7 mg.

Analytical Runs using Third Component

The solid phase is however likely to retain a certain amount of the saturated solution which will not be separated from the solid by the centrifugal force employed and the presence of the solution will decrease the percentage of gold in the solid phase below the true value. The amount of solution remaining on the solid can be determined by a method mentioned by Bancroft¹⁷ and also described and used by van Heteren,¹⁸ namely the addition of a third component which will not be in the crystals but will be in the solution. Then from the amount of the third component found in the solid phase, the amount of solution retained can be calculated and so the true value for the composition of the crystals can be calculated.

The substance chosen as a third component must be present only in the liquid phase. If the component is not to be in the solid phase it must not form a solid solution with the solid phase nor may it form a compound which is stable at the temperature used. The only way possible to choose such an element is to suppose that a metal which does not form solid solutions in gold and does not form a stable compound with gold probably will not form solid solutions or compounds with the solid phase whatever it may be. Thallium^{12a} is a metal which fulfills these requirements since pure gold separates from liquid gold-thallium solutions of concentrations up to 72% thallium and at all temperatures down to the eutectic which is 120°C. Lead^{12b} is also of interest since pure gold separates from gold-lead solutions from 0 to 45% lead above 436°C, which is the temperature of decomposition of the compound Au₂Pb. Lead does not form solid solutions in gold and if the eutectic of the compound Au₂Pb with the solid phase of the gold-mercury system is at a temperature below 300°, the solid phase in equilibrium with solutions containing only small amounts of lead with gold and mercury at 300° would contain no lead.

In order to use this method it was necessary to develop a method of analyzing mixtures for the three metals used. A sample of thallium was obtained which was said to contain about 2% of carbon and seemed also to contain some volatile matter. Since it did not alloy properly with gold and mercury its use was abandoned. Lead from a certified Bureau of Standards sample, stated to contain less than 0.05% impurity, was used and knowns were prepared by heating the ternary systems in sealed glass tubes until they were completely fused. The knowns were then cooled and trans-

ferred from the tubes to weighed porcelain crucibles. The mercury was removed from the gold and lead by heating the crucibles for several hours at from 300° to 350°C, thus slowly vaporizing most of the mercury and avoiding spattering, and then continuing the heating at 550°C for several hours. It was necessary to use a non-oxidizing atmosphere (such as hydrogen) to prevent the formation of lead oxide which is more volatile than lead and would probably vaporize. Lead is not lost since its vapor pressure reaches 0.001 mm. of mercury only at 636°C.¹²⁰

The first method tried for removing the lead was to volatilize it from a porcelain crucible using an oxygen-gas flame. Upon heating with the flame the lead oxidized and while some of the oxide volatilized more of it fused into the porcelain and could not be removed. It was however found possible to get rid of all the lead by heating the gold-lead residue on a bone-ash cupel up to the melting point of gold. Here again the heating had to be done carefully to prevent spattering. The lead oxide formed during the heating was absorbed by the bone ash, leaving a button of pure gold. If the gold was heated very much above its melting point it volatilized but by heating just to the melting point good results were obtained. The data for two knowns analyzed in this way are given in Table IV.

TABLE IV
Analysis of Knowns for Gold, Mercury, and Lead

		Taken	Found	Error
I	g.Au	2.9537	2.9528	low 0.9 mg.
	g.Hg	1.0606	1.0584	low 2.2 mg.
	g.Pb	0.0254	0.0271	high 1.7 mg.
II	g.Au	2.1796	2.1808	high 1.2 mg.
	g.Hg	0.8464	0.8444	low 2.0 mg.
	g.Pb	0.1160	0.1161	high 0.1 mg.

Since the amount of lead present in the solid phase, which is used to calculate the amount of saturated solution left behind on the crystals, is small (15 to 20 mg. in our runs) a small absolute error in the determination of the amount of lead results in a large error in the calculated amount of solution left behind and therefore a sizable error in the corrected percentage of the solid phase. Thus for one tube it was calculated that a difference of one mg. in the amount of lead found in the solid phase would cause a difference of 3/4% in the calculated gold concentration of that phase. The percentages given for the composition of the solid should not therefore be considered any more precise than plus or minus one even if the assumption that the pure solid phase contains no lead is true. There is nothing, however, to indicate that this assumption is not true.

The runs in which lead was used were carried out in exactly the same manner as the earlier runs, except for the method of analysis. A check on the accuracy of the analyses was made by comparing the total amount of

each constituent found in both phases with the amount put in the tube at the beginning. The greatest differences in the four tubes in which lead was used were as follows: for gold 19.6 mg. low, for mercury 23.3 mg. low, and for lead 9.4 mg. low. All of the results for gold and mercury were low but for lead half were high. The average errors (not regarding sign) were as follows: gold 17.5 mg., mercury 14.6 mg., and lead 4.0 mg. Despite the fact that the lead was determined by difference the absolute accuracy of its determination was greater than that for gold or mercury.

Analytical Runs—Results

The results of the analytical runs are given in Table V. Runs A through E using gold and mercury alone seem to show that at temperatures from 295 to 359°C the solid phase in equilibrium with saturated solutions of gold in mercury has a composition somewhere between 60 and 80% gold. There is no indication of a change in the composition of the solid phase in the temperature range investigated.

TABLE V

Gold and Mercury alone

Run no.	Temp. °C	Liquid Phase			Solid Phase		
		Au gms.	Hg gms.	At. % Au	Au gms.	Hg gms.	At. % Au
A-I ^a	307.9*	2.4561	9.6403	20.58	0.9608	0.9069	51.87
A-II ^a	do	2.1580	8.7699	20.01	2.0269	1.0632	65.98
B-I ^b	359.3*	2.9379	5.2585	36.24	2.5454	0.8701	74.84
B-II ^b	do	2.0289	3.4864	37.17	1.8300	0.8444	68.80
C-I ^a	359.2*	2.5896	4.1770	38.69	1.5241	1.0198	60.33
C-II ^a	do	1.7517	2.8032	38.87	1.0221	0.7196	59.10
D-I ^c	297.2*	2.0697	12.0023	14.92	1.1274	0.2305	83.27
D-I ^c	do	(2nd part of solid phase)			0.8300	0.5374	61.11
D-II ^c	do	0.6292	3.4231	15.75	0.5895	0.1173	33.83
E-I ^d	295.8	1.0064	5.9344	14.71	1.1173	0.7003	61.88
E-II ^d	do	0.9598	5.8167	14.37	1.1556	0.3777	75.68

Gold, Mercury, and Lead

Run no.	Temp. °C	Liquid Phase			Solid Phase			
		Au gms.	Hg gms.	Pb gms.	Au gms.	Hg gms.	Pb gms.	At. % Au Corrected
F-I ^b	317.1	2.5091	3.7221	0.5657	0.4319	0.2021	0.0146	77.89
(F-II ^b)	do	2.0844	2.9922	0.5251	1.4024	0.2292	0.0179	91.4)
G-I ^a	317.1	1.9718	2.7920	0.5422	1.7271	0.6118	0.0162	76.25
G-II ^a	do	2.5216	3.6239	0.6941	2.0138	0.5730	0.0268	81.82
Average (F-II out)								78.65
Average deviation:								26.8 p.p.t.

* See footnote to Table II.

^a From high side.

^b From low side.

^c Some strips of gold were never dissolved.

^d The shaft showed a tendency to stick which made the centrifuging poor.

Runs F and G using gold, mercury, and lead gave much more concordant results for the composition of the solid phase corrected for the amount of solution retained. If we leave out F—II (the deviation of which from the average of the other three is more than four times the average deviation of the other three) the results give an average value of 78.65 at. % with an average deviation of 26.8 parts per thousand which is about what might be expected from the precision of the analytical method.

Synthetic Runs with the Reconstructed Furnace

A number of runs of the synthetic type were also made with the reconstructed furnace as is indicated in Table II. The main difference in procedure caused by the change in the furnace was that in determining the solubility point the bath was adjusted so that the temperature was rising slowly and filtrations were made periodically rather than keeping the temperature constant at each tenth of a degree for several minutes and then moving up a tenth of a degree when it seemed clear there was solid left. The change in procedure was necessitated by the fact that the lag in the new furnace from the time the heat was increased until the temperature started to rise was of the order of ten minutes.

It happened regularly with a few tubes and once in a while with most of the rest that, after inverting the tube the liquid would not completely filter off through the capillary, leaving the solid behind. When some of the liquid remained above the capillary it was almost impossible to tell whether or not any solid was left. After the furnace had been changed so that the tubes could be whirled it was found that the last part of the liquid could be forced through the capillary by revolving the tubes. Since the whirling left the solid in a rather packed condition, which was moreover practically the same after each filtration, it was possible to estimate the solubility temperature from the amounts of solid left in the tube at two temperatures below the solubility point. These estimates speeded the accurate determination of the solubility point.

Some of the difficulties in applying the synthetic method of solubility determination to this system should be pointed out. The difficulties encountered if any mercury oxidizes have been mentioned. Any small foreign bodies in the tubes such as pieces of glass are also objectionable because they may get caught in the capillary and retard or entirely prevent filtration.

If any considerable number of fine crystals which pass through the capillary are present the solubility temperature determined will be too low. In runs made by the analytical method the systems are held for a long time at constant temperature and undoubtedly the crystals all grew to such a size that they would not pass through a capillary. Since the results of the synthetic method check those of Weiner³ and of Mees⁴ determined by the analytical method and since the present analytical results lie at lower rather than higher temperatures than the synthetic curve it does not seem probable that an error was introduced by fine crystals passing through the capillary.

If temperature differences exist in the parts of the furnace through which the tube passes as it is rotated, the possibility arises that parts of the tube may be at times hotter than other parts. It might then happen that by some particular manipulation of the tube the contents would be heated for a time enough to dissolve all the solid (when the amount of solid present is small) without any change having occurred in the temperature of the bath. If on subsequent cooling, which would result when the rocking was resumed, the system persisted in a supercooled liquid state, the result would be that the

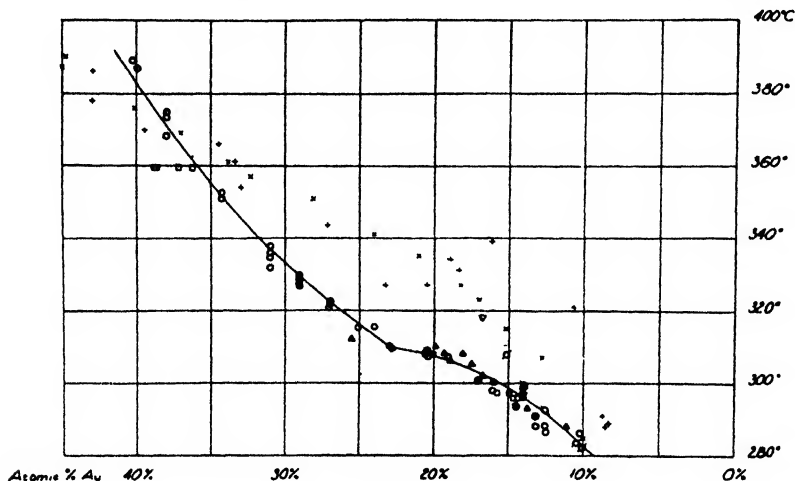


FIG. 4

○ Anderson, synthetic; □ same, analytical; φ Sunier and Mees; ⋈ Sunier and Weiner; Δ Parravano; + Britton and McBain; × Plaksin; ▽ Eastman and Hildebrand.

temperature found as the solubility point would be too low. The different results obtained in running the same tube on different days was attributed at least in part to this cause. For that reason the highest result was in general considered the nearest to the correct value.

Discussion of Results—Solubility

The solubility of gold in mercury has been determined at temperatures up to 300°C in this laboratory by Weiner³ and by Mees.⁴ The results of the present investigation below 300° agree well with theirs, as can be seen on the graph Fig. 4. Another set of determinations which are in substantial agreement with those found in this laboratory are those of Parravano,⁶ determined by the cooling curve method. The solubility over the entire range covered has also been determined by Britton and McBain⁸ and by Plaksin.¹¹

Britton and McBain made their determinations by an analytical method. They find a maximum in the solubility curve at about 14.3% of which there is no indication in the present results. At that concentration their curve is 40° higher than the curve of Fig. 4. Plaksin found the solubility by the method of cooling curves. His solubility curve does not have a maximum but is a

smooth curve lying partly above and partly below that of Britton and McBain. Both the curves of Britton and McBain and of Plaksin lie above the curve of Fig. 4 from 280° to about 370° and below at higher temperatures.

Eastman and Hildebrand⁵ investigated the vapor pressures of solutions of gold in mercury at about 318°C and found that the vapor pressure decreases as the concentration of gold increases up to 16.8 at. % gold and thereafter remains constant. This means that a saturated solution of gold in mercury at 318° contains 16.8 at. % gold. This value agrees best with Plaksin's results, lying more than 10° higher than the curve of Fig. 4.

The greatest difference in temperature for a given composition in the present data is about 6° and the average deviation of the synthetic points from the curve is 2.2°C . The nature and precision of the data allow some freedom in locating the break in the curve. The temperature of the break, which is the temperature of some change in the solid phase, is to be considered accurate only to within plus or minus 10° .

Discussion of Results—Compounds existing

Parravano⁶ investigated the gold-mercury system below 312° by the method of cooling curves and found a compound Au_2Hg_3 (40 at. % Au) which decomposes at about 100°C forming Au_3Hg (75 at. % Au). Braley and Schneider⁷ working also by the method of cooling curves found the compounds AuHg_4 (20 at. % Au), Au_2Hg_5 (28.6 at. % Au), and AuHg (66.7 at. % Au). They found a thermal effect at about 100° as Parravano did and also one at about 380° . If we assume that their rate of cooling was much too rapid to allow equilibrium to be established (they state that the longest arrest was 180 sec.) their results giving a maximum in the liquidus curve might possibly be interpreted as being due to a thermal effect at about 300°C . The results given by Braley and Schneider for the liquidus curve for low gold concentrations are not even in the right neighborhood. There is evidently something very wrong with their work and the existence of the compounds reported by them is not well established.

Britton and McBain⁸ determined the solubility curve for gold in mercury by an analytical method and found a maximum in the curve at about 14.3 at. % Au which led them to postulate the compound AuHg_6 with a congruent melting point of 342°C .

Plaksin¹¹ by the method of cooling curves in a research apparently of considerably greater precision than either that of Braley and Schneider or of Parravano found the compounds AuHg_2 (33.3 at. % Au) and Au_2Hg (66.7 at. % Au). He states that AuHg_2 has transition points at -36° and at 122° and decomposes into Au_2Hg and a liquid phase at 310° . Au_2Hg undergoes a polymorphic transformation at 402° and breaks up into a liquid solution of gold in mercury and a saturated solid solution of Au_2Hg in gold at 420° . This means that there are thermal effects at 420° , 402° , 310° , 122° , and at -36° . These are to be compared with the effects found by Parravano and by Braley and Schneider at 100° and by the latter authors also at 380° and possibly at 300° . The break in the solubility curve found in this investigation

at about 310° is also an indication that there is at that temperature a change of some kind in the solid phase involving a heat change. Plaksin confirmed his conclusions by metallographic methods.

Biltz and Meyer⁹ investigated the vapor pressures of gold-rich amalgams of varying compositions at three temperatures, 253° , 300° , and 315° . They interpreted their results as showing the existence, in addition to the solid solution in pure gold upon which all investigators agree, of a solid solution of compositions from 75.6 to 79.3 at.% Au. This would seem to necessitate the existence of a compound in that composition range, the simplest formula for which would be Au_7Hg_2 . If the lowest gold concentration were 75.0% instead of 75.6% the probability would be that the compound Au_3Hg (75.0 at.% Au) exists and forms solid solutions with gold but not with any constituent containing less than 75% Au. Fixing the limit of the solid solution range appears to depend on locating the point of inflection of the vapor pressure-composition curve and therefore might be wrong by a small amount. Biltz and Meyer further state that mixtures having less than 75% Au have the vapor pressure of pure mercury. This seems to disagree with the results of Eastman and Hildebrand⁴ who found that at $318^{\circ}C$ the vapor pressure of a saturated solution of gold in mercury is only about 0.93 of the vapor pressure of pure mercury. Nevertheless the results of Biltz and Meyer may be interpreted as showing that between 253° and 315° only one compound of gold and mercury exists and that it has a composition between 75 and 80 at.% Au and forms a solid solution.

Pabst¹⁰ investigated the gold-mercury system by the powder method of x-ray analysis. He found a hexagonal phase at about 75% Au which he believes is the same as the solid solution phase which Biltz and Meyer say exists between 75.6 and 79.3 at.% Au. He also found evidence of compounds existing at room temperature of the formulas Au_2Hg_3 (40 at.% Au) and $AuHg_2$ (33.3 at.% Au). That the latter compound exists seems improbable since he states that by putting an amalgam of less than 33% Au in a leather bag and squeezing with a screw clamp, mercury is removed to such an extent that the compound Au_2Hg_3 is formed. With regard to the usefulness of the x-ray analysis method it is of interest that in the related system silver-mercury Murphy²⁰ found that this method gave results when no conclusions could be drawn from photomicrographs and the cooling curve method failed because of the slowness of attainment of equilibrium.

The present results as well as those of Biltz and Meyer, of Pabst, and of Parravano indicate that the gold rich compound formed is probably Au_3Hg instead of Au_2Hg as reported by Plaksin and by Braley and Schneider. Both the present investigators and Biltz and Meyer fail to find evidence of a second compound poorer in gold below 310° , the present work going down to 295° and that of Biltz and Meyer down to 253° . That a second compound is formed at lower temperatures seems likely but whether it is $AuHg_2$ as found by Plaksin or Au_2Hg_3 as reported by Parravano and by Pabst is not clear. The existence of more than two compounds in the system at room temperature or above does not seem probable.

A Suggested Phase Diagram for the System Au-Hg

Fig. 5 gives the phase diagram for gold and mercury constructed by Plaksin¹¹ and Fig. 6 presents a new phase diagram suggested for the same system. It is really an extension of the diagram constructed by Parravano⁶ who gave the compounds shown but did not say anything about solid solution formation nor about anything in the region above 300°C. Parravano gave the temperature of decomposition of Au_2Hg_3 (40 at.% Au) as 100° but his individual values varied over more than 10°. The value of 122° used in Fig. 6 is the tem-

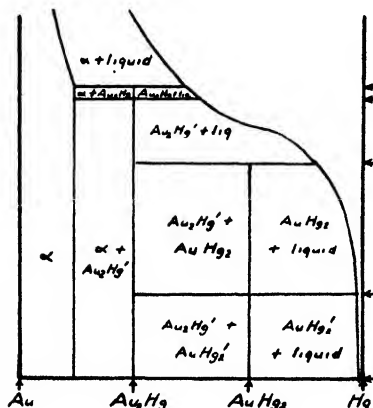


FIG. 5
According to Plaksin

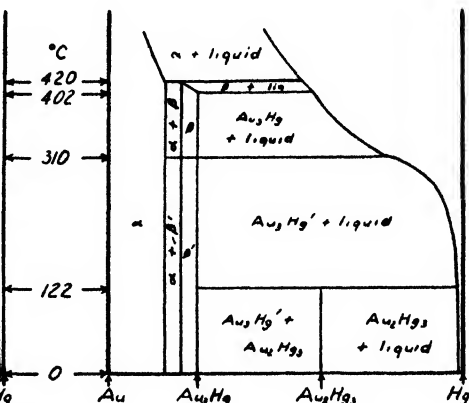


FIG. 6
A Suggested Phase Diagram
Phase Diagrams of the System Au-Hg.

perature given for a thermal effect by Plaksin¹¹ who, however, says that the effect is caused by an allotropic change in the compound AuHg_2 (33.3 at.% Au). That the compound reported by Parravano, Au_2Hg_3 , is the one existing is supported by the results obtained by Pabst using the x-ray analysis method. The temperatures of the other thermal effects are those given by Plaksin and the one given at 310° is also indicated by the break in the curve of Fig. 4.

Fig. 6 also differs from Plaksin's phase diagram in showing the compound Au_2Hg_3 and indicating that it dissolves gold to form the beta solid solution. The existence of the compound Au_2Hg_3 (75 at.% Au) instead of that reported by Plaksin, Au_2Hg (66.7 at.% Au), is supported by the work of Parravano, of Biltz and Meyer,⁹ and of Pabst¹⁰ as well as by the results of the analytical runs as given in Table V. The thermal effect at 310°, which Plaksin interprets as caused by the decomposition of the compound AuHg_2 , is shown as caused by an allotropic change of the compound Au_2Hg_3 . This effect will therefore extend through all the regions in which the compound itself or the solid solution of gold in it (the beta solid solution) occurs. The temperature of the change must be constant through the two phase areas (alpha plus beta) and (Au_2Hg_3 plus liq.) but would in general change in passing through the beta solid solution area instead of being constant as shown, since the transformation temperature would in general be a function of the gold concentration of the solid solution.

The transformation in the beta area probably would take place also over a range of temperature and the shape of the curves might have any of the forms found in the corresponding change from liquid solution to solid solution. It will be noticed that the phase diagram of Fig. 6 is in accord with the results of the analytical runs given in Table 5 in that no change in the composition of the solid phase in equilibrium with the saturated solutions is indicated at 310° . Plaksin's diagram demands that the composition change at that temperature from 33% Au to 67% Au. It is also evident that the two diagrams demand different values for the composition at which the cooling curve break at 310° is maximum. Fig. 5 has the maximum break come at 33.3 at.% corresponding to a complete change of solid and liquid into the compound AuHg_2 , while Fig. 6 places it at 75 at.% at which composition the whole system, being the compound Au_3Hg , undergoes the polymorphic change.

The thermal effects at 402° and at 420° Plaksin's diagram shows are due, respectively, to a polymorphic transformation and the decomposition of the compound Au_2Hg . Fig. 6 shows that, starting with the compound Au_3Hg and heating, the decomposition of the solid phase into beta solid solution and liquid begins at 402° and continues gradually, with no invariant point, to 420° , where the remaining beta solid solution being now saturated with gold decomposes at constant temperature into saturated alpha solid solution and liquid. It will be noticed that, if the diagram is correct, when a sample is being cooled the change in the solid phase at 402° is not a discontinuous one accompanied by a heat change, which according to the phase rule must take place at constant temperature, as is the case at 420° , and at 310° , and at 120° . Rather the change in the solid phase, the beta solid solution, lies in the fact that at 402° its composition reaches that of the compound Au_3Hg at which value it ceases to change, thereafter remaining constant as the temperature is lowered. The break found in a cooling curve therefore would not be a horizontal line, but simply a change in slope such as occurs at the liquidus point. There is no experimental evidence which indicates that the break at 402° should be as shown in Fig. 6 rather than as shown in Fig. 5. The form of diagram shown in Fig. 6 is however, a possibility.

Plaksin's phase diagram, Fig. 5, rests on cooling curve and metallographic results. When using the cooling curve method and even more particularly when using the metallographic method it is important that equilibrium be attained in the process, otherwise the results can not in general be interpreted. Murphy²⁰ in his work with the system silver-mercury found with one sample that it was necessary to anneal for three days at 100°C in order that equilibrium be attained, as indicated by a maximum liberation of heat at the invariant point at 127°C . With another sample he found that the complete formation of the beta phase in a good crystalline form from the alpha phase and liquid required annealing at 100° for four weeks (as shown by photomicrographs). If the gold-mercury system is like the silver-mercury system in this respect it seems likely that to successfully analyze the system by these methods would require uncommon care.

Fig. 6 is to be considered as a phase diagram which seems to fit the results of Parravano, Biltz and Meyer, Pabst, and of the present investigation better than does the diagram given by Plaksin. The two highest singular points, however, are given only by the evidence of Plaksin whose work stands alone in the region except for the point at 380° advanced by Braley and Schneider.⁷

The present knowledge about the system gold-mercury can not be considered satisfactory. An independent determination of the liquidus curve above 300° would be valuable. More evidence as to what compounds exist and what their regions of stability are is to be desired. Additional carefully conducted thermal and microscopic experiments very likely would help solve the problem.

The writer wishes to express his thanks to Prof. Conley for his aid in the explanation of the work of Plaksin, and to acknowledge his indebtedness to Prof. Sunier, who has so charitably and inspiringly directed this investigation.

Summary

(1) The application of the synthetic method of solubility determination to a metallic system has been made. A form of solubility tube with a capillary filter has been developed which enables the disappearance of the solid phase to be detected when the solution is not transparent.

(2) Using this method 42 determinations of the solubility of gold in mercury have been made between 280° and 400°C .

(3) The uniformity of temperature in an air bath at temperatures of 300° to 400°C has been investigated and the variations of temperature in the center part found to be about one degree.

(4) Methods of analysis have been found for mixtures of gold, mercury, and lead.

(5) A tube has been designed in which the liquid phase is separated from the solid by filtering through a porous glass disc. The tube is mounted on a shaft and whirled and the centrifugal force causes the filtering. Using this tube ten analytical runs have been made with gold and mercury between 295° and 360°C in which the solid and liquid phases were separated and the composition of each determined.

(6) Four similar analytical runs have been made in which some lead was added to the gold and mercury and, by assuming that all the lead found in the solid phase represents an equivalent amount of solution which has not been removed by the centrifugal force, a corrected composition of the solid phase has been calculated.

(7) The solubility results agree with the results of Sunier and Weiner, Sunier and Mees, and Parravano but do not agree well with those of Britton and McBain and of Plaksin. The solubility curve shows a break at about 310°C , at which temperature Plaksin also reports a thermal effect.

(8) The results found for the composition of the solid phase indicate that the gold-rich compound is probably Au_3Hg instead of Au_2Hg as found by

Plaksin. A suggested phase diagram is given which seems to agree with the results of Parravano, Biltz and Meyer, Pabst, and the present work better than does the phase diagram given by Plaksin.

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THE DIFFUSION OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS

BY L. J. BURRAGE

I. Introduction

The main object of the present investigation was to test the accuracy with which the diffusion coefficients of electrolytes could be measured as a preliminary to work on the diffusion of mixtures. Comparison was made with the results of Öholm, which form the most accurate and extensive work on the subject so far available. The experimental comparison was carried out on sodium chloride, partly in order to ascertain whether there was a definite minimum in the diffusion coefficient-concentration curve similar to those found in the cases of HCl, KCl and LiCl. Whereas Öholm¹ found such minima to be well marked with these electrolytes, the curve for sodium chloride was practically linear between 1 M and 6 M, and parallel to the concentration axis, exhibiting no upward movement. Its course in this concentration region was, however, determined by two points only, at 2.8 M and 5.5 M, and these are scarcely sufficient for so large a concentration range. In the experiments recorded below the diffusion coefficient has been determined for six solutions falling within the same range; the curve can consequently be drawn with greater accuracy. Figures have also been obtained for the diffusion coefficient of 0.1 M HCl in water and these have been made use of in a later paper where experiments on the rate of diffusion of 0.1 M HCl in solutions of alkali metal halides are described.

II. Experimental

An examination of the previous workers' methods and the difficulties which they experienced, shows that there are three important factors which must be taken into account to ensure the success of the practical work.

- (a) Temperature Variation.
- (b) Vibration Effects.
- (c) Mixing during the filling or emptying of the apparatus.

Although, strictly speaking, these three factors come under the one category, since they all cause a false movement of the diffusing substance, it will be advantageous to consider them separately and to show what precautions have been observed to eliminate each.

(a) *Temperature Variation.*

A sudden rise or fall in the temperature tends to cause mixing of the solution even though that variation be comparatively small. A much greater temperature change will be far less serious if it takes place over a long period of time.

¹ Z. physik. Chem., 50, 309 (1904).

In order to reduce this temperature effect to a minimum the experiments were carried out in a large vault, the door of which was felted to prevent any possibility of draughts. The vault itself had a fairly constant temperature, the maximum range covered being 12°C . in Winter to 18° in Summer.

The vault was lit by a single electric lamp which was used as little as possible during the experiments, an electric torch also being used when a strong local illumination was needed. The author remained in the vault for as short a time as possible during an experiment.

Inside this vault, whose only outlet was the door, was a large wooden box six feet in height and three feet square in cross-section, papered throughout internally and then painted, thus ensuring that all cracks and pinholes were covered. The parts of the box which opened were felted, both inside and outside, to prevent any slight external temperature change from being communicated. The box was provided with maximum and minimum thermometers.

(b) *Vibration Effects.*

In order to ensure that the vibration effects should be reduced to a minimum the following precautions were taken.

A vibration-free concrete block was constructed which stood about 3 feet above the ground level and was $2\frac{1}{2}$ ft. square in cross-section. On this a stout wooden platform was securely bolted and so arranged as to be exactly horizontal.

This block was entirely encased by the constant temperature box to which reference has already been made. A portion of the front, the whole width and 18 inches high, was hinged at its lower end and thus allowed of access to the apparatus when emptying the latter. In order to avoid opening this door unnecessarily it was fitted with a long mica inspection window about 3 inches in height and running the whole length near the bottom.

(c) *Convection effects during the filling or emptying of the apparatus.*

A full description of the apparatus employed will be given at this point, as the design is a matter of importance when discussing convection effects during filling or emptying.

An examination of previous workers' apparatus has brought to notice the following points:

(1) That a very accurate control of the rate of flow of the liquid is necessary when filling or emptying, and

(2) That it is preferable to fill from above and empty from below.

The method employed in this investigation was based upon that of Graham as modified by Svedberg and Öholm. In general outline it consisted of placing a certain volume of solution below three times that volume of pure water and allowing diffusion to take place. At the close of the experiment the liquid was separated into four equal portions which were referred to as layers. These were analysed and the distribution of substance in each of the layers obtained.

The apparatus used in these experiments was essentially that of Öholm.¹ It consisted of a diffusion cylinder D about 20 cms. long and 3.5 cms. in cross-

¹ Z. physik. Chem., 50, 309 (1904).

section, fitted with a ground glass joint at the upper end and a capillary tube, 1.5 mm. in diameter, with tap, at the lower. A is a pipette of about 20 ccs. capacity between the marks x and y, and fitted with taps above and below these points. Below the lower tap was a ground glass joint B, which fitted into the diffusion cylinder. In this ground glass joint there was a small hole C to allow of the free passage of air during filling or emptying.

The length of capillary tubing below E was 0.5 mm. in diameter. This was an improvement on previous designs, which did not employ a sufficiently narrow capillary. A second point of difference between this apparatus and that used by Öholm was the incorporation of a tap at the top of the pipette. This tap was so adjusted as to let air pass very slowly indeed. Both these improvements were designed to minimize mixing of the solution when the diffusing liquid first entered the diffusion cylinder. Unless very careful control is exercised when the lower tap is first turned the diffusing liquid will run down into the cylinder too rapidly and convection will result.

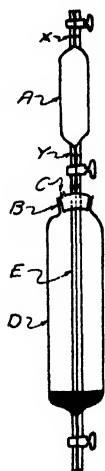


FIG. 1

(d) *Method of Operation.*

(1) *Filling.* Four pieces of apparatus were arranged side by side near the front of the box and mercury poured into each until it was 0.5 mm. — 1.0 mm. below the end of the pipette. Each pipette was then filled to the upper mark with distilled water placed in the apparatus, and allowed to run in until the liquid reached the lower mark. This was repeated twice. The diffusion cylinders were now corked and the pipettes put on a stand at the back of the box, which was closed and left for about 24 hours to allow of temperature equalisation.

Each pipette was then rinsed out with the solution whose diffusion coefficient was about to be determined, filled to the top mark, the stem being carefully dried with a dry cloth, and inserted in the apparatus. The door of the box was closed and the apparatus left for 3 hours to allow the disturbing effects of slight change of temperature, due to opening the door of the box, and liquid disturbances, caused by the withdrawal of the pipette, to disappear.

After a three-hour interval the door of the box was opened and the lower tap turned very slowly, the time being simultaneously noted, for diffusion starts from this moment. The speed of running-in was such that the total 20 ccs. should take about 2 hours. The rate was noted by the movement of the liquid column, observation being made through the upper of the mica windows. When the liquid had reached the lower mark the tap was turned and the door of the box closed. The vault was not entered again until the time for the withdrawal of the liquid had arrived. The length of a single run varied from case to case, but generally fell between one and seven days.

(2) *Withdrawal of the Liquid.* A narrow platform, fitted inside the box, ran parallel to the front, underneath the exit tubes at the bottom of each piece of apparatus. It was attached to the sides of the box, was quite independent

of the concrete block, and served as a tray to carry the flasks which were filled with liquid during emptying.

The liquid was drawn off into flasks of similar design to those used by Öholm, each one having a graduation mark on the neck corresponding to the volume of the pipette, between the marks *x* and *y*. In this way the liquid column could be separated into four equal portions, which were subsequently analysed.

The time was noted when each flask was filled, the period of diffusion being counted up to this point. It was most essential that the four layers should be separated as accurately as possible, since a very slight error at this point caused a large variation in the determined value of the diffusion coefficient.

The rate at which the withdrawal of the liquid was carried out was approximately 1 cc. per 10 mins., although considerably longer times have been taken in some cases.

(e) *Materials employed.*

The following chemicals were involved in this investigation:—

(1) Potassium and Sodium Chlorides. These were of A.R. quality and were used as such after heating strongly until all decrepitation had ceased.

(2) Hydrochloric Acid. Analytically pure acid was distilled under constant boiling conditions. This was then diluted until a concentration of exactly 0.1 M was obtained.

(3) Lithium Chloride. This was not obtainable as A.R. quality. The impurities, other than water, were, however, only a few hundredths of 1%, the chief being ferric chloride.

(f) *Calibration of the Apparatus.*

The calibration of each portion of the apparatus was carried out with water, by weighing in the case of the pipette and volume measurements for the cylinder.

For the success of the experiments it is essential that the diffusion column should be as nearly as possible of constant cross-section. This means that the diffusion cylinder must be of constant cross-section as must also be the external dimensions of the capillary of the pipette.

The cylinder was calibrated in the following manner. It was set up in the stand, as for an experiment, mercury being run in until there was about a millimetre gap between this and the end of the pipette. The height of this mercury level was read off, the measurements being made to 1/100 mm. by a cathetometer. A known volume of water — 9.94 ccs. — was then added and the level of the water measured with the pipette in position and when it had been removed. This was carried out eight times successively. The results showed that in every case, the condition of constancy of cross-section was sufficiently fulfilled.

III. Results

The diffusion coefficient has been calculated for each of the four layers from the tables of Kawalki and Stefan.¹ In Table I a few results are given showing the agreement between the coefficients for the four layers for sodium chloride solutions.

The vertical columns have the following significance:—

1. Concentration of sodium chloride.
2. Temperature of experiment.
3. The Diffusion coefficient for the lowest layer.
4. The Diffusion coefficient for the next layer and similarly for 5 and 6.
7. The average diffusion coefficient of all four layers. Each horizontal set of figures shows the complete results for one single experiment.

TABLE I

1 Conc.	2 T	3 K ₁	4 K ₂	5 K ₃	6 K ₄	7 av K
0.498 M.	13.6°	0.936	0.931	0.933	0.932	0.933
		0.937	0.917	0.948	0.945	0.937
		0.931	0.943	0.938	0.930	0.935
		0.935	0.946	0.943	0.927	0.938
5.810 M.	13.5°	0.952	0.945	0.953	0.949	0.950
		0.954	0.960	0.952	0.949	0.954
		0.951	0.952	0.952	0.946	0.950
		0.954	0.955	0.952	0.955	0.952

Table II comprises the full results and the symbols have the following significance.

- M. Weight molality.
- A. Apparatus used.
- T. The temperature of the experiment °C.
- Δt. The extreme temperature variation.
- K. The average diffusion coefficient for the four layers.
- K¹. The average diffusion coefficient for a given concentration at a definite temperature.

¹ Wied. Ann., 52, 166 (1894).

TABLE II

M	A	T	Δt	K	K ¹
0.1012	A	14.7	— .7	0.989	
	B	14.7	— .7	0.989	
	E	14.7	— .7	0.977	
	F	14.7	— .7	0.990	0.986
0.198	D	13.6	— .5	0.936	
	A	13.6	— .5	0.952	0.944
	C	14.4	— .5	0.969	
	F	14.4	— .5	0.964	
	B	14.4	— .5	0.970	0.968
0.498	D	13.6	— .2	0.933	
	F	13.6	— .2	0.937	
	A	13.6	— .3	0.935	
	B	13.6	— .3	0.938	0.936
1.005	C	13.6	— .3	0.927	
	F	13.6	— .3	0.926	
	B	13.6	± .0	0.929	0.927
	A	13.0	± .0	0.912	0.912
1.501	A	13.7	— .3	0.930	
	D	13.7	— .3	0.928	
	C	13.7	— .3	0.937	
	B	13.7	— .3	0.926	0.930
2.072	D	15.0	+ .4	0.972	
	E	15.0	+ .4	0.974	
	F	15.0	+ .4	0.954	
	A	15.0	— .6	0.992	0.973
	D	12.8	+ .1	0.897	
	F	12.8	+ .1	0.913	0.905
2.936	C	13.5	± .0	0.917	
	D	13.5	± .0	0.918	0.918
	A	13.8	+ .1	0.954	
	C	13.8	+ .1	0.947	0.950
4.259	D	13.3	+ .3	0.930	
	F	13.3	+ .3	0.920	
	C	13.3	+ .3	0.947	
	B	13.3	+ .3	0.925	0.930

Table II (continued)

M	A	T	Δt	K	K ¹
5.503	A	16.0	+ .3	1.026	1.026
	B	17.0	+ .6	1.075	1.075
	D	13.3	+ .05	0.940	
	F	13.3	+ .05	0.939	0.940
5.810	A	13.5	\pm .0	0.950	
	B	13.5	\pm .0	0.954	
	F	13.5	\pm 0	0.950	
	C	13.5	\pm .0	0.954	0.952
Hydrochloric Acid					
0.1004	B	16.2	- .1	2.153	
	A	16.2	+ .3	2.157	
	B	16.2	+ .3	2.156	
	C	16.2	+ .5	2.148	2.153
	F	16.6	- .3	2.166	2.166

The variation in the temperature during the course of the experiment (Δt) only amounted to 0.1 – 0.2°C., the increase above this value being caused by the opening of the box at the close of the experiment, thereby exposing the apparatus to the change in the temperature of the vault. The Δt values quoted in the table represent the change which had occurred at the close of each experiment and that amount due to the opening of the box cannot affect the result to any serious extent as the diffusion had already proceeded for a period varying from 1 to 7 days, and the gradient must be small, hence there is little danger of any sudden connection effect due to this cause, since it only occurs during the withdrawal of the liquid.

IV. Discussion

Discussion of Sources of Errors affecting the Results.

(a) The first possibility is that the amount of diffusing substance in the column may be increased during a run by diffusion out of the end of the pipette. This, however, does not take place since the lowest section of the bottom layer in the diffusion column does not change in concentration during the course of the experiment, and there is therefore no tendency for the pipette contents to diffuse outwards. However, if any did diffuse, it would not cause serious error since the volume of liquid contained in the pipette below the lower tap is exceedingly small.

(b) It will be noted that the value of K derived from the second layer of an experiment sometimes appears high. This is undoubtedly due to a very slight amount of mixing. A reference to Kawalki's figures will show how serious is the effect of a slight error in the determination of the amount of

diffusing substance in this particular layer. There will be seen that the value of v' , the amount of substance expressed as parts per 10,000, for the second layer very slowly increases and then falls just as slowly. This gives a very flat curve corresponding to a large range of x values, where $x = h^2/KT = \frac{1}{2}$ height of a layer squared, divided by the diffusion coefficient multiplied by the time. It is thus easy to see that a very slight error in v' may give rise to a very serious error in the value of x and thus cause the value of K to be somewhat inaccurate.

(c) In some cases the value of the K for the fourth layer is somewhat uncertain. This happens when the experiment has only proceeded for a short space of time and there is an insufficient amount of diffusing substance in the top layer to give a really accurate analysis.

Comparison of Results at 18°

The results in Table II have been calculated to 18°C. by means of the temperature coefficients given by Öholm¹ and these final figures are collected in Table III together with those obtained by Öholm. Fig. 2 contains the data (circles) for NaCl plotted in the form of diffusion coefficient against molality. Öholm's data are shown by crosses.

TABLE III

Substance	M	K 18°	Öholm K 18°
NaCl	0.101	1.094	1.117
	0.198	1.086	1.089
	0.498	1.078	1.077
	1.005	1.069	1.074
	1.501	1.067	—
	2.072	1.071	—
	2.936	1.074	1.064
	4.259	1.083	—
	5.503	1.097	1.065
	5.810	1.100	—
HCl	0.100	2.227	2.229

Agreement with Öholm is seen to be moderate throughout the whole concentration range. In contrast to his results, however, the present curve shows a distinct minimum at a concentration of 1.5 M.

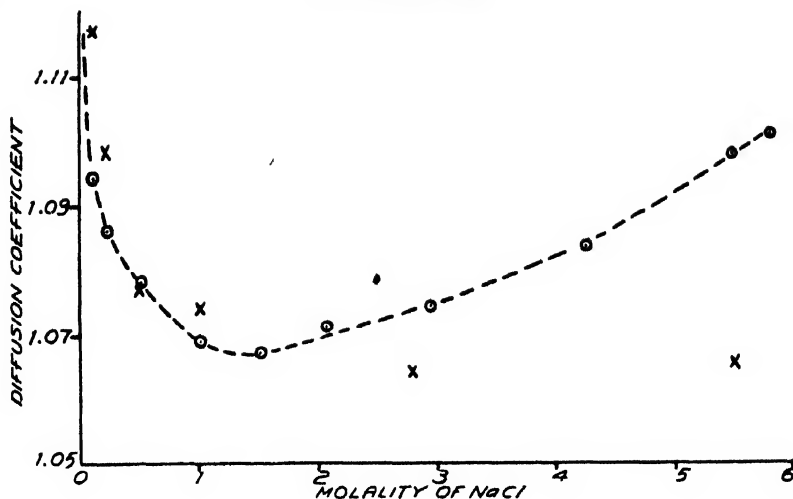


FIG. 2

Summary

- I. A detailed account has been given of the precautions taken to prevent vibration and mixing.
- II. The diffusion coefficient of NaCl has been measured over a large concentration range.
- III. The diffusion coefficient of 0.1 M HCl has been measured.
- IV. Comparisons have been made with existing data.

The author desires to express his thanks to Prof. A. J. Allmand, under whose direction this work has been carried out.

*King's College,
University of London.
March 17, 1932.*

ELECTRODEPOSITED ϵ -BRASS

BY H. KERSTEN* AND JOSEPH MAAS†

Introduction

The crystal structure of brass made by fusing together zinc and copper has been the subject of a number of investigations¹ which have shown that such brass probably has five different structures (known as α , β , γ , ϵ , and η), all stable at room temperature.

Alloys of zinc and copper have been electrodeposited from mixtures of their cyanides dissolved in a solution of potassium or sodium cyanide, since 1841.² It has recently been shown that α -brass having a structure agreeing with that of a fused alloy of like composition may be deposited from such a solution.³ This paper shows that ϵ -brass, agreeing reasonably well in composition and structure with fused ϵ -brass may also be deposited from a cyanide bath.

Experimental

The electrolysis was carried on in a one-liter beaker with stainless steel anode and cathode, each 5×10 cm in size, 5 cm apart. The sides of the anode and cathode not facing each other were covered with a thick sheet of celluloid so that no current could flow from the back of the anode or to the back of the cathode. Stainless steel was used as an anode because it was practically insoluble in the electrolyte and as a cathode because the deposit did not adhere well and could be stripped for analysis.

A bath having the following composition was made:

Zinc cyanide.....	40 gm,
Sodium cyanide.....	50 gm,
Sodium carbonate.....	30 gm,
(anhydrous)	
Water, to make.....	1 liter

To this was added small quantities of copper cyanide to determine a region in which the ϵ -brass could be deposited. A new bath was used for each sample plated. For all the experiments the current density was held at 2 amperes per square decimeter and the bath temperature at 50°C.

The x-rays were supplied by a gas tube⁴ having an iron target. The samples were clamped in the reflection spectrograph⁵ shown in Fig. 1, in which the x-rays, after passing through the slits in the tube at the left, strike the

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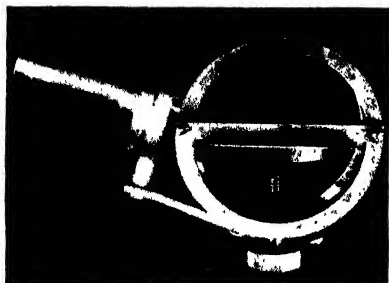


FIG. 1
X-ray spectrograph.

sample clamped at the center of the ring, diffract into smaller beams, and blacken a photographic film in a paper envelope held on the circumference of the large ring by means of a rubber band.

Conclusions

The percentage of copper in the deposit from a number of baths made by adding copper cyanide to the bath given in a previous paragraph is given in Table I.

TABLE I

Bath number	Gm of CuCN in the bath	Percentage of copper in the deposit	Bath number	Gm of CuCN in the bath	Percentage of copper in the deposit
1	0.75	5.9	5	1.70	18.7
2	1.25	9.4	6	1.70	21.4
3	1.50	11.4	7	1.80	25.1
4	1.50	19.6	8	2.00	20.5

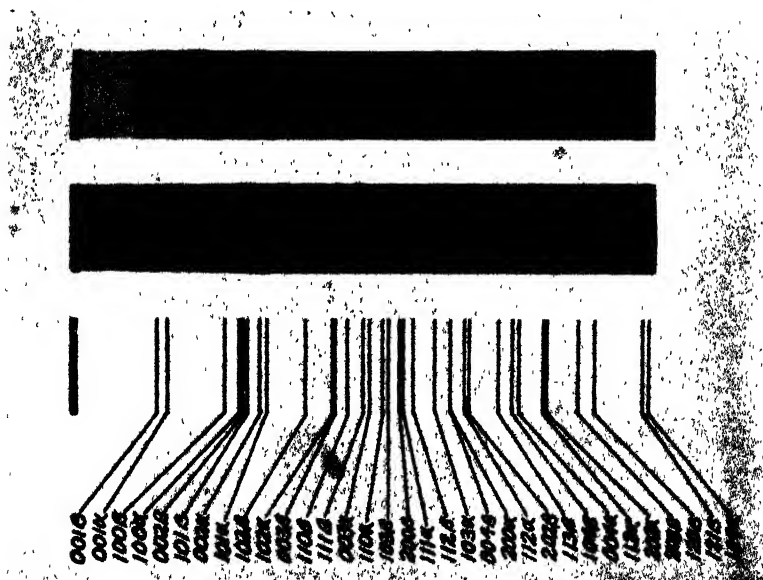


FIG. 2

Electrodeposited ϵ -brass compared with fused ϵ -brass.
 Top: Electrodeposited sample containing 18.7% copper.
 Middle: Fused sample containing 16.13% copper.
 Bottom: Computed position of the lines for 19.7% copper.

Samples 3, 4, 5 and 6 showed the ϵ -structure. Fig. 2 shows the reflection photograph for sample 5 compared with fused ϵ -brass of nearly the same composition and with the computed positions of the diffraction lines. The fused ϵ -brass was annealed for 9 days at 360°C, before the picture was taken.

It is evident that the two photographs show structures nearly the same. The electrodeposited sample did not give as sharp lines as the annealed fused sample. Some of the lines to be seen on the original negatives have been lost in the reproduction.

The authors wish to express their thanks to Dr. Earl F. Farnau for the loan of samples of fused brass of various compositions.

References

- ¹ References are given in Wyckoff: "The Structure of Crystals," 2nd. Ed., 212 (1931).
- ² Gore: "The Art of Electro-Metallurgy," 278 (1877).
- ³ Nakamura: Sci. Papers Inst. Phys. Chem. Research (Tokyo), **2**, 287-92. (1925).
- ⁴ Kersten: Rev. Sci. Inst., **3**, 145-50. (1932).
- ⁵ Kersten: Rev. Sci. Inst., **3**, 384 (1932).

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES

III. Exchange Adsorption during the Coagulation of Hydrous Oxide Sols

BY HARRY B. WEISER AND GEORGE R. GRAY

"Superequivalent" Displacement of Chloride

In recent communications¹ a method of procedure has been given which enables one to follow the displacement of chloride ion from the micelles of hydrous oxide sols during the stepwise addition of coagulating electrolyte. The method of titration previously described in detail consists essentially in mixing separate portions of sol, in which is suspended a small amount of calomel, with gradually increasing amounts of electrolyte and determining the chloride concentration potentiometrically after the mixture has stood in a thermostat for at least 48 hours to allow equilibrium conditions to be established. The significance of these observations and of the accompanying change in hydrogen ion concentration, for the precipitation process, have received detailed consideration in the earlier papers and will not be reviewed here.

Rabinowitsch² followed a much simpler method of titration: A definite portion of sol containing suspended calomel was placed in a beaker containing mercury, thus making one-half of a calomel concentration cell. The other half was a standard calomel electrode. The difference in potential was measured at the outset and shortly after each addition of a small amount of coagulating electrolyte. This procedure, which has the advantage of being more rapid than the one we adopted, leads to entirely different results as indicated by the two curves shown diagrammatically in Fig. 1. The lower curve *W* representing the displacement of chloride by sulfate was obtained with a hydrous Fe_2O_3 sol by the method used in this laboratory³ while the upper curve *R* was obtained on a similar sol by Rabinowitsch and Kargan.⁴ It will be noted that the former curve follows a smooth course well below the straight line showing the amount of sulfate added, while the initial portion of the Rabinowitsch curve lies above the sulfate line indicating that with low concentrations of coagulating agent, appreciably more chloride is displaced than corresponds to the sulfate added. Similar observations were made by Wassiliev and Rabinowitsch with Al_2O_3 sol but the phenomenon appeared less frequently than with Fe_2O_3 sol.

¹ Weiser: J. Phys. Chem., **35**, 1, 1368 (1931).

² Rabinowitsch and Kargan: Z. physik. Chem., **133**, 203 (1928); Wassiliev and Rabinowitsch: Kolloid-Z., **56**, 306 (1931).

³ Weiser: J. Phys. Chem., **35**, 16 (1931).

⁴ Z. physik. Chem., **133**, 203 (1928).

The so-called "superequivalent" displacement of chloride ion during the titration process was at first believed by us to be a delusion resulting from the slowness with which the calomel electrode comes to equilibrium. Rabinowitsch, on the other hand, is of the opinion that this factor is relatively unimportant and defends his experimental method. After stating that he has confirmed the experimental results reported by us, he writes:¹

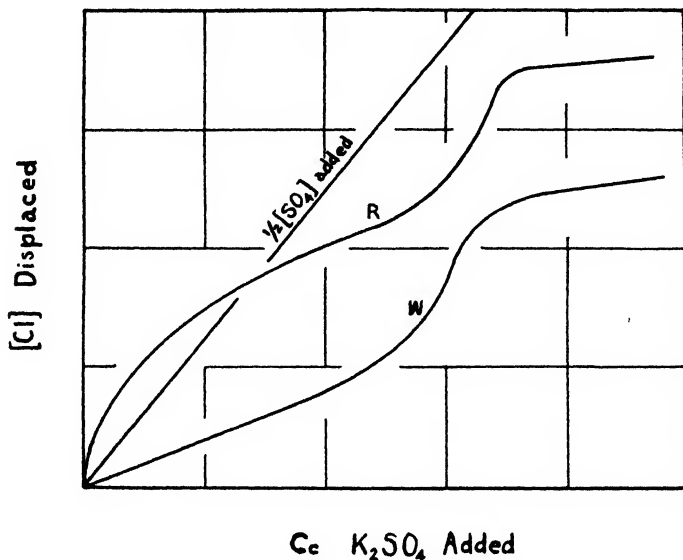


FIG. 1

Diagrammatic Representation of Chloride Displacement Curves obtained on "Titrating" Fe_2O_3 Sols with K_2SO_4 by the Method of Weiser (W) and Rabinowitsch (R).

"There is only one point of discrepancy between your views and those of my laboratory. It regards the question of legitimacy of the procedures used in our respective laboratories. I think that both are equally legitimate. Of course yours presents a more close approximation to the equilibrium in each point of the curve. But ours, which has the advantage of rapidity and simplicity, is no less satisfactory. It only gives the picture of the changes which take place in the first minutes and hours after the addition of each portion of electrolyte, whereas yours tends to find the final state of the system.

"The irregular trend of the potentiometric titration curve in our experiments which you ascribe to the calomel electrode not attaining the state of equilibrium, we understand as the picture of the stormy processes of ionic interchange following immediately the addition of concentrated electrolyte solutions to the colloid."

¹ Private communication to Harry B. Weiser. A similar point of view is expressed in an article which appeared after this paper was written. [Rabinowitsch and Fodiman: *Z. physik. Chem.* 159A, 403 (1932)].

This is not convincing for it leaves altogether unanswered the nature of the "stormy process of ionic interchange" which brings about the alleged superequivalent displacement of chloride ion.

Adsorption of Precipitating Ions

In the investigations above referred to, attention has been given especially to the stepwise displacement of chloride resulting from the adsorption of the precipitating ion. The converse of this procedure consists in determining the actual amount of precipitating ion adsorbed during the stepwise addition of electrolyte both above and below the precipitation value. This has been done by Peterson and Storks¹ for the adsorption of chromate by hydrous alumina. A series of samples of the Al_2O_3 sol was prepared by the addition of varying amounts of K_2CrO_4 and the adsorption determined by the change in concentration. Below the precipitation value, the sol was ultrafiltered and the ultrafiltrate analyzed, while above the precipitation value, an aliquot part of the supernatant solution was withdrawn for analysis. A curve showing three distinct parts was obtained. The first part, below the precipitation value, was characterized by decreasing adsorption with increasing concentration of electrolyte while above the precipitation value the curve had a form similar to that of the usual adsorption isotherm but with a distinct point of inflection. Peterson and Storks believe that the first portion of the curve represents a neutralization adsorption, the last portion a surface adsorption non-electrical in type, and the intermediate portion a combination of the two types.

Since the adsorption of the precipitating ion by hydrous Al_2O_3 prepared from the chloride is an exchange adsorption process throughout most, if not all, of the concentration range investigated, the observations of Peterson and Storks may be open to question. Indeed both the choice of precipitating reagent and the experimental method appear to be somewhat unfortunate. In the first place, it is known that the following equilibrium is set up in chromate solutions: $2\text{CrO}_4^{--} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{--}$. In such solutions we are dealing with two ions and when they are mixed with the sol there will be a shift in the equilibrium depending on the change in pH value.² In the second place, nothing can be told about the true adsorption equilibrium after ultrafiltration. The process causes a gradual change in the amount of intermicellar solution in contact with the micelles and results in more or less coagulation and agglomeration of the micelles, especially if it is carried very far. A potentiometric method which does not involve ultrafiltration may give a fairly accurate measure of the concentration of ions in equilibrium with those adsorbed in the micelles; but the true equilibrium will be shifted by ultrafiltration.

In this investigation attention will be given to the two questions raised in the above survey: (1) the alleged superequivalent displacement of chloride

¹ J. Phys. Chem., **35**, 649 (1931).

² Cf. Weiser and Middleton: J. Phys. Chem., **24**, 648 (1920); Ishizaka: Z. physik. Chem., **83**, 97 (1913); cf., also, Weiser: J. Phys. Chem., **35**, 1368 (1931).

ion from a hydrous oxide sol by a precipitating electrolyte; and (2) the interrelation between adsorption of a precipitating ion and displacement of chloride during the stepwise addition of electrolyte to a hydrous oxide sol.

I. "Superequivalent" Displacement of Chloride Ion

The hydrous oxide sols of aluminum, chromium and iron were "titrated" with K_2SO_4 by means of the Rabinowitsch method. The observations disclose the causes of the observed superequivalent displacement of chloride and indicate the unsatisfactory nature of the rapid Rabinowitsch procedure.

General Method of Procedure

Preparation of Sols. Al_2O_3 Sol I was obtained by adding 1.5 *N* NH_4OH from a dropping funnel to 1 liter of a solution containing 100 g $AlCl_3 \cdot 6H_2O$ stirred by a mechanical stirrer, until the precipitate which first formed just failed to redissolve. The mixture was diluted to 3 liters, boiled for 30 minutes and dialyzed in a Neidle¹ dialyzer at 75° until a satisfactory ratio of Al_2O_3 : Cl was obtained, after which it was evaporated to the desired concentration and allowed to age. Al_2O_3 Sol II was formed by the method of Wassiliev and and Rabinowitsch:² 75% of the theoretical amount of 7.5 *N* NH_4OH was added with constant stirring to 1 liter of solution containing 100 g of $AlCl_3 \cdot 6H_2O$. The mixture was diluted to 1750 cc and dialyzed as above described.

The Cr_2O_3 sol was prepared by adding to 1 liter of solution containing 55 g $CrCl_3$, small portions at a time of NH_4OH containing 25 g of concentrated base diluted to 800 cc. The mixture was diluted to 3.5 liters, boiled for 30 minutes, and dialyzed in a Neidle dialyzer at 75°.

The Fe_2O_3 sol was made by adding dilute NH_4OH in small portions to 500 cc of a solution containing 100 g $FeCl_3 \cdot 6H_2O$, until 75% of the amount necessary for complete precipitation was used. The sol was diluted to 3.5 liters, dialyzed at room temperature to remove the excess $FeCl_3$ and finally at 75° until the desired ratio of Fe_2O_3 to Cl was obtained.

TABLE I
Age and Composition of Hydrous Oxide Sols

Sol	Age before use	Composition	
		M_2O_3 g/l	Cl equivalents/l
Al_2O_3 I	3 months at room temperature	5.08	0.0206
Al_2O_3 II	3 months at room temperature	3.53	0.0268
Cr_2O_3	2 months at room temperature	6.02	0.0140
Fe_2O_3	2 weeks at 80° + 1 month at room temperature	5.91	0.0096

¹ J. Am. Chem. Soc., **38**, 1270 (1916).

² Kolloid-Z., **56**, 306 (1931).

The oxide content of the several sols was determined by precipitating with a slight excess of NH_4OH , filtering, washing, and igniting in the usual way. The chloride content was gotten by adding a slight excess of AgNO_3 and then a large excess of HNO_3 followed by digestion in the dark for 24 hours at 80° . This dissolved the hydrous oxide and after dilution, the AgCl was filtered into a Gooch crucible, washed, dried and weighed. The age before use and the composition of the several sols are summarized in Table I.

Method of Titration. The change in chloride ion concentration during the stepwise addition of $0.5\text{ }N\text{ K}_2\text{SO}_4$ was determined by the method of Rabinowitsch and Kargan¹ using the same potentiometer set-up and electrode vessels previously described.² In all cases, 15 cc of sol were used and $0.5\text{ }N\text{ K}_2\text{SO}_4$ was added from a micro burette graduated in 0.01 cc . The potential was measured against a $0.1\text{ }N$ calomel electrode and the chloride activity as KCl was calculated by means of the Nernst equation. The molar concentration was obtained from activity by means of a graph prepared from data given by Lewis and Randall.³ The chloride concentration was corrected for dilution by the added electrolyte.

Preliminary experiments showed that electrodes prepared with sols not previously saturated with calomel required 12 to 15 hours before constant potentials were obtained, while sols which had stood in contact with calomel overnight usually gave constant potentials within 3 hours. Accordingly the electrodes were prepared at least 12 hours before the titration was begun.

The titration proceeded as follows: The electrolyte was added from the burette to the sol in the electrode vessel and the mixture stirred thoroughly with a stirring rod. The potential against the $0.1\text{ }N$ electrode was read at 10-minute intervals for 30 minutes and then at 15-minute intervals until the potential was constant for three consecutive readings. In general, the alumina sols gave a constant potential after 30 minutes to one hour, while a somewhat longer time was required for the chromic oxide sol and a still longer time for the ferric oxide sol. Above the coagulation point the potential became constant after 10 to 30 minutes.

Experiments with Alumina Sol

Preliminary observations with alumina sol disclosed that there was no superequivalent displacement of chloride if the sol was thoroughly mixed with electrolyte and a reasonable time allowed for the electrode to come to equilibrium conditions. Rapid mixing of sol and electrolyte in an all-glass mixing vessel gave mixtures which showed no evidence of superequivalent displacement of chloride ion at any concentration.

It was observed that the dropwise addition of the relatively strong electrolyte to the sol causes localized coagulation. If stirred sufficiently vigorously, the precipitated hydrous oxide is peptized completely; but if the

¹ Z. physik. Chem., 133, 203 (1928).

² Weiser: J. Phys. Chem., 35, 8 (1931).

³ "Thermodynamics," 344, 362 (1923).

TABLE II

Titration of Al_2O_3 Sol I with 0.5 N K_2SO_4

	K_2SO_4 0.5 N cc	milli- volts	(αCl) $\times 10^3$	[Cl] $\times 10^3$	[Cl] corrected $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{2}[\text{SO}_4]$ added $\times 10^3$
	0.00	57.1	8.46	9.05	9.05	0.00	
A	0.05	44.0	14.14	15.62	15.67	6.62	1.67
B	0.05	51.4	10.58	11.54	11.57	2.52	1.67
C	0.05	54.5	9.18	9.92	9.95	0.90	1.67
A	0.10	41.3	15.72	17.48	17.62	8.57	3.33
B	0.10	51.2	10.66	11.68	11.76	2.71	3.33
C	0.10	53.4	9.78	10.62	10.69	1.64	3.33
A	0.20	40.8	16.03	17.86	18.09	9.04	6.67
B	0.20	48.6	11.81	12.96	13.13	4.08	6.67
C	0.20	49.5	11.40	12.50	12.66	3.61	6.67
A	0.30	42.6	14.94	16.54	16.86	7.81	10.00
B	0.30	45.0	13.60	15.00	15.30	6.25	10.00
C	0.30	46.1	13.02	14.35	14.64	5.59	10.00
A	0.40	45.8	13.18	14.48	14.86	5.81	13.33
B	0.40	44.6	13.81	15.25	15.64	6.59	13.33
C	0.40	44.9	13.65	15.02	15.41	6.36	13.33
A	0.50	45.3	13.44	14.85	15.30	6.25	16.67
B	0.50	44.0	14.14	15.62	16.18	7.13	16.67
C	0.50	42.5	15.00	16.62	17.12	8.07	16.67
A	0.60	41.4	15.66	17.40	18.09	9.04	20.00
B&C	0.60	41.4	15.66	17.40	18.09	9.04	20.00
A	0.70	40.2	16.41	18.30	19.14	10.09	23.33
B&C	0.70	40.9	15.97	17.78	18.52	9.47	23.33
A	0.80	40.0	16.54	18.44	19.39	10.34	26.67
B&C	0.80	40.7	16.10	17.90	18.85	9.80	26.67
A	0.90	39.9	16.61	18.50	19.58	10.53	30.00
B&C	0.90	40.3	16.35	18.18	19.26	10.21	30.00

mixture is not well stirred or if sufficient time is not allowed before making the chloride ion measurement, a value appreciably above the normal equilibrium value would be expected. That such is the case is indicated by the following experiments.

Effect of the Nature of the Stirring following the Dropwise Addition of Electrolyte. The 0.5 N K_2SO_4 was allowed to drop into 15 cc of sol from a micro burette and the following observations made at 23° : A. The mixture was stirred gently for a few seconds after which it was allowed to stand 10 minutes and the potential measured against an $N/10$ calomel electrode.

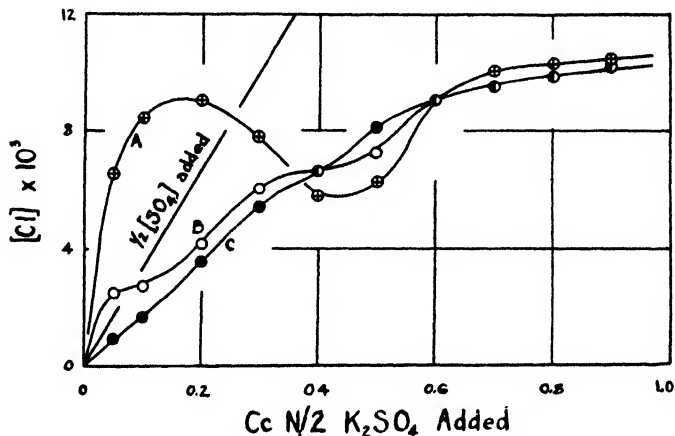


FIG. 2

"Chloride Displacement" Curves with Al_2O_3 Sol I (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

B. The mixture was then stirred vigorously for 30 seconds, allowed to stand for 10 minutes and the potential read once more. C. The mixture was again stirred thoroughly and potential readings taken at 10 minute intervals until three consecutive readings were the same. The observations on Al_2O_3 Sol I are given in Table II and shown graphically in Fig. 2. Line A shows the values obtained on the first reading, line B on the second, and line C the final value.

Observations with Al_2O_3 Sol II are given in Fig. 3. The results are similar to those of Sol I in all essential respects.

It is apparent that the chloride concentrations calculated from the first potential readings show very erratic variations from the equilibrium conditions. The observed superequivalence is the result of two errors inherent in the method, which render it of questionable value. First, the partial coagulation accompanying the addition of strong electrolyte results in a proportionately greater displacement of chloride than if no coagulation takes place. This relatively greater displacement of chloride in the zone of coagulation accounts for the marked change in direction of the equilibrium chloride displacement curve in this region.¹ Second, a few minutes is insufficient time

¹ Cf. Weiser: J. Phys. Chem., 35, 10, 1374 (1931).

for the sol-calomel-electrolyte mixture to come to equilibrium. Accordingly the curve obtained by adding the relatively strong solution to the sol, stirring gently, and measuring after 10 minutes, is meaningless.

The second curve obtained after thorough stirring and waiting for an additional 10 minutes is more regular and the observed superequivalence is much less. Here also the superequivalence results chiefly from partial electrolyte coagulation which is not completely reversed and from delay in setting up equilibrium at the electrode. The final equilibrium curve is similar in form to those obtained by Weiser's method but the true amount of chloride dis-

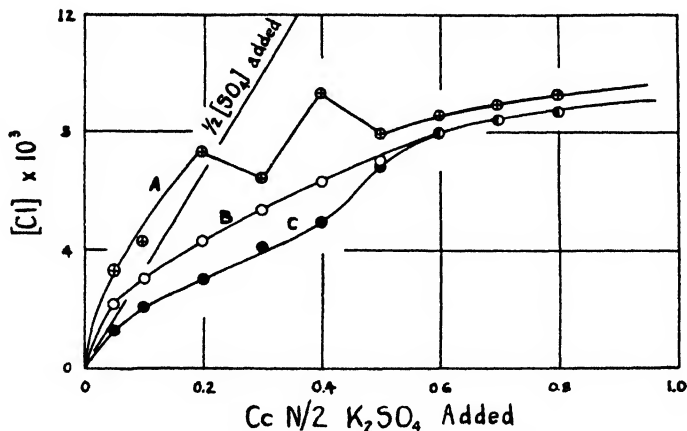


FIG. 3

"Chloride Displacement" Curves with Al_2O_3 Sol II (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

placed is uniformly higher. The reason is obvious. In the Rabinowitsch method, partial coagulation always takes place below the precipitation value, while this is avoided in Weiser's procedure. The excess chloride displaced by the partial coagulation is never taken up completely since the coagulation is not completely reversible.

From these observations it is clear that the Rabinowitsch method of procedure has little to commend it. Initial coagulation is distinctly objectionable and the titration curves are meaningless unless an approximate state of equilibrium is attained. If time is allowed for this, the procedure is much more time consuming than the Weiser method. Thus, starting with the sol saturated with calomel, approximately 15 hours elapsed from the beginning of the titration until the last point in the C curves of Figs. 2 and 3 were obtained. In the Weiser method about two hours are required to prepare the series of electrodes containing the varying amounts of electrolytes and after these have stood for 2 days to attain equilibrium, the potentiometric measurements are made in a few minutes. Moreover, the method of mixing avoids the complication of localized coagulation below the precipitation value.

Effect of Concentration of Sol. Since the so-called superequivalent displacement of chloride ion results in part from an inherent error in the experi-

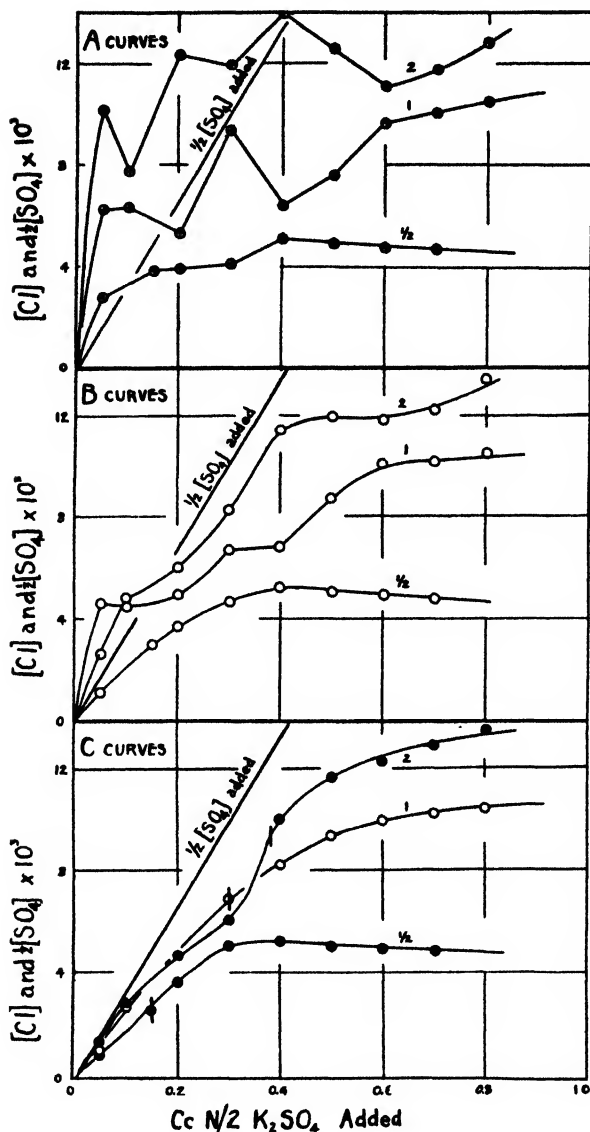


FIG. 4

"Chloride Displacement" Curves with Al_2O_3 Sols of Varying Concentration (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

mental method, namely, partial electrolyte coagulation, it follows that the effect would be least marked the greater the dilution of sol. This is borne out by the following experiments: Al_2O_3 Sol I was evaporated in a vacuum desiccator over H_2SO_4 until its concentration was approximately doubled. Titration experiments similar to those described in the preceding section were then made on (1) the concentrated sol (2) the concentrated sol diluted with one part of water and (3) the concentrated sol diluted with three parts of

water. In order to conserve space the lengthy tables of data are omitted but the results are shown graphically in Fig. 4. To avoid confusion the *A*, *B* and *C* curves for three different sols are plotted separately. The results speak for themselves. There is no "superequivalent" displacement with the most dilute sol if the sol electrolyte mixture is thoroughly stirred before making the potentiometric reading. This merely confirms the earlier observations in this laboratory that there is no indication of superequivalent displacement when the sol is mixed rapidly with the highly diluted precipitating electrolyte.

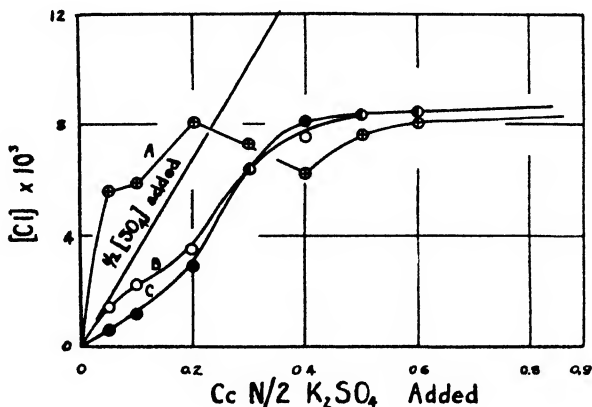


FIG. 5

"Chloride Displacement" Curves with Cr_2O_3 Sol (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

In this connection attention should be called to the observation of Rabino-witsch and Kargan¹ that the excess of chloride ion displaced, falls off with dilution of sol and disappears entirely with five-fold dilution of a Fe_2O_3 sol whose original concentration was 5.76 grams per liter. This is as it should be but the reason for this behavior was apparently overlooked.

Experiments with Chromic Oxide Sol

Observations on the Cr_2O_3 sol were made by the same procedure used with alumina and the results are shown graphically in Fig. 5. The similarity of curves obtained under similar conditions with the two different sols is at once apparent.

Experiments with Ferric Oxide Sol

The observations with Fe_2O_3 sol are so similar to those with Al_2O_3 and Cr_2O_3 that no comment is necessary. The data are shown graphically in Fig. 6. Since the chloride content of the sol is less than in the other two sols the chloride displacement is correspondingly less. For this reason the scale in Fig. 6 is made twice as large as in the other figures.

¹ Z. physik. Chem., 133, 224 (1928).

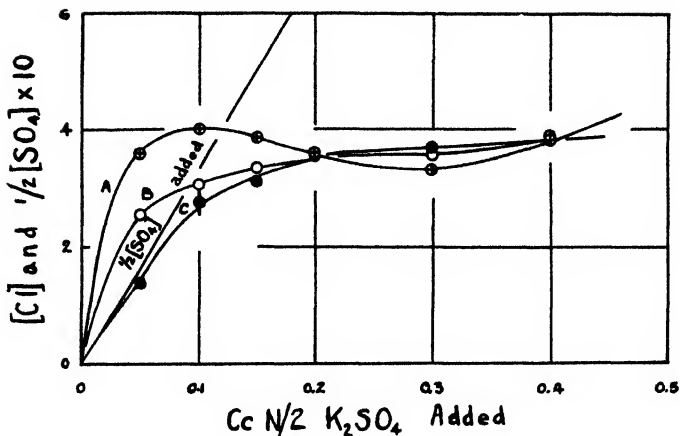


FIG. 6

"Chloride Displacement" Curves with Fe_2O_3 Sol. (A) after 10 minutes, (B) after 20 minutes and (C) at equilibrium.

Conclusion

The conclusion from these observations is that the so-called superequivalent displacement of chloride ion during the "rapid" titration of hydrous oxide sols by the dropwise addition of a relatively strong precipitating electrolyte according to the method of Rabinowitsch, is the result of an unsatisfactory experimental procedure which produces localized coagulation of a portion of the sol and does not allow time for equilibrium conditions to be approached. It is not typical of any one sol and the experimental conditions cannot be developed uniformly in any case. For this reason the chief value of the rapid procedure is in emphasizing the experimental conditions which should be avoided in studying the change in the adsorption equilibria which follow the stepwise addition of precipitating electrolytes to sols.

II. Adsorption of Precipitating Ions

It will be recalled that Peterson and Storks obtained a curve showing three distinct parts for the adsorption of chromate added in gradually increasing amounts to alumina sol. Since the equilibrium curves showing the displacement of chloride from hydrous oxide micelles by adsorption of sulfate and other ions including chromate, show no breaks,¹ there was no reason for believing that breaks would occur in the adsorption curve of the precipitating ion. The following experiments indicate that there are no breaks in the adsorption curves for sulfate added stepwise to the hydrous oxide sols of aluminum, chromium and iron.

General Procedure. It was found by preliminary experiments that all of the precipitation concentration of sulfate was adsorbed by the several oxides. Since none of the precipitating electrolyte was left over at the precipitation point, it is apparent that none would remain unadsorbed below the precipitation value. Accordingly, it was necessary to make the adsorption measure-

¹ Weiser: J. Phys. Chem., 35, 1, 1368 (1931).

ments above the precipitation value only. This was fortunate since, as we have seen, it is not permissible to ultrafilter the sol and since the lead sulfate electrode was found to be unsatisfactory for the potentiometric estimation of low concentration of sulfate.

A definite amount of 0.5 *N* K₂SO₄ was added from a micro burette graduated in 0.01 cc to 15 cc of sol contained in a test tube. The tube was stoppered and the mixture shaken thoroughly. After standing 24 hours the precipitated hydrous oxide was thrown down by centrifuging for 30 minutes at 3000 r.p.m. in an International Equipment Company Centrifuge. The supernatant liquid was poured off and centrifuged 15 minutes more, after which an aliquot part was analyzed for sulfate by the nephelometric method which was found by preliminary experiments to be quite satisfactory.

To a mixture of 5 cc of 1% BaCl₂ solution, 5 cc of 0.1 *N* HCl and 1 cc of 5% sulfate-free gelatin,¹ was added an amount of liquid (not exceeding 5 cc) which contained not over 0.5 mg of SO₄ ion as determined by preliminary experiment, and the final volume was made up to 16 cc with water. This sample was compared with a standard prepared at the same time using 5 cc of K₂SO₄ solution containing 0.24 mg SO₄. The comparison was made after the sample had stood 15 minutes, using a Dubosque-Leitz nephelometer. In each case the mean value of 10 readings was taken.

Adsorption by Alumina. The measurements of adsorption by alumina was accomplished without difficulty except at concentrations just above the precipitation value. In this region traces of alumina that are shaken up during the centrifuging process remain in suspension persistently. Accordingly, the determination of unadsorbed sulfate after the addition of 0.3 and 0.35 cc of K₂SO₄ was made by the following modification of the procedure described above: A 2 cc sample of the supernatant liquid was added to a mixture of 5 cc of 0.1 *N* HCl, 5 cc H₂O, and 0.5 cc 1% BaCl₂ solution. Another 2 cc portion was added to a similar mixture in which water was substituted for the BaCl₂

TABLE III
Adsorption of Sulfate by Al₂O₃ Sol I
(15.0 cc of sol with 0.5 *N* K₂SO₄)

K ₂ SO ₄ 0.5 <i>N</i> cc	SO ₄ added mg	SO ₄ in solution mg	SO ₄ adsorbed mg	$\frac{1}{2}$ [SO ₄] adsorbed × 10 ³	$\frac{1}{2}$ [SO ₄] corrected × 10 ³	$\frac{1}{2}$ [SO ₄] added × 10 ³
0.30	7.20	0.61	6.59	8.98	9.16	10.00
0.35	8.40	1.23	7.17	9.73	9.95	11.67
0.40	9.60	1.48	8.12	11.00	11.29	13.33
0.50	12.00	1.74	10.26	13.80	14.21	16.67
0.60	14.40	2.44	11.96	15.97	16.60	20.00
0.70	16.80	3.30	13.50	17.92	18.76	23.33
0.80	19.20	4.31	14.89	19.63	20.67	26.67
0.90	21.60	5.80	15.80	20.70	21.94	30.00

¹ Denis and Reed: *J. Biol. Chem.*, **71**, 193 (1926).

solution. These samples were compared with a standard prepared at the same time containing 0.12 mg SO_4 . The samples were allowed to stand 15 minutes before making the comparison. A correction for the turbidity due to dispersed Al_2O_3 was applied to the calculated SO_4 concentration.

The observations are recorded in Table III and shown graphically in Fig. 7, together with the chloride displacement curve from Fig. 2.

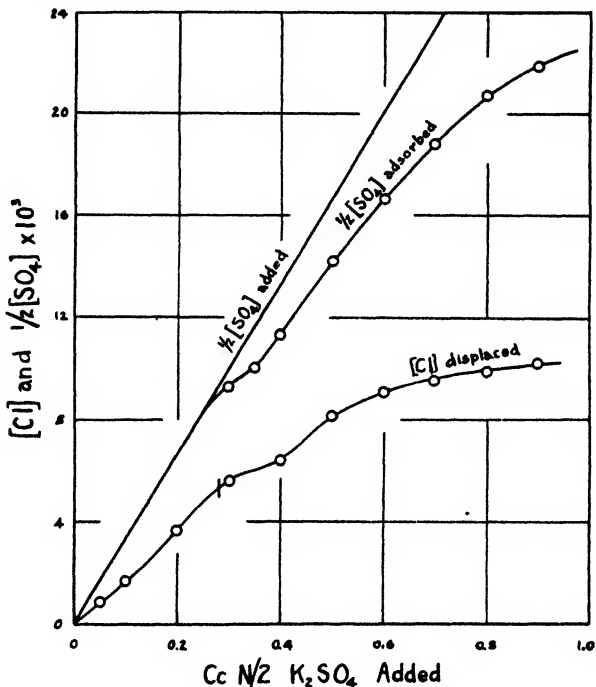


FIG. 7

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Al_2O_3 Sol. I.

The sulfate concentration was corrected to the same basis as the chloride displaced, *i.e.*, to 15 cc volume. The adsorption curve follows an unbroken course through the entire concentration range, but there appears to be a slight point of inflection just above the precipitation value corresponding to a similar bend in the chloride displacement curve. The sulfate adsorption is appreciably greater than the amount of chloride displaced. The reason for this is that a part of the sulfate which is taken up corresponds to chloride measurable potentiometrically in the intermicellar solution.¹

Adsorption by Chromic Oxide. No difficulty was encountered in the adsorption measurements with Cr_2O_3 sol since the supernatant solution above the precipitation value was entirely free from suspended matter. The adsorption data are given in Table IV and the adsorption is shown in Fig. 8 together with the chloride displacement curve from Fig. 5.

¹ Cf. Weiser: *J. Phys. Chem.*, **35**, 23, 1392 (1931).

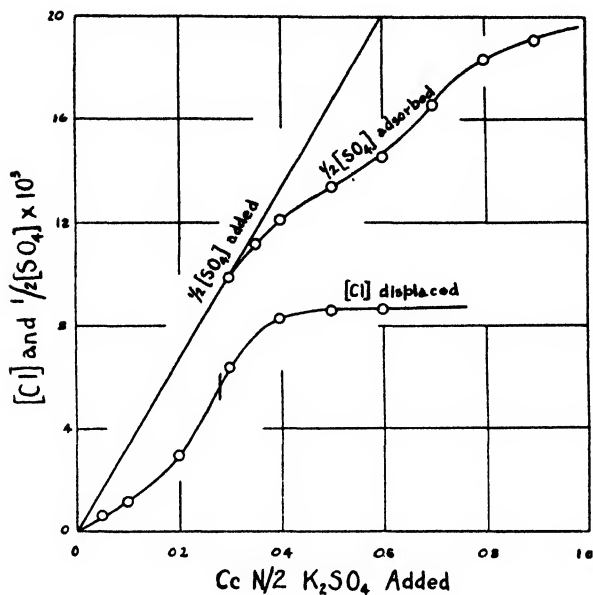


FIG. 8

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Cr_2O_3 Sol.

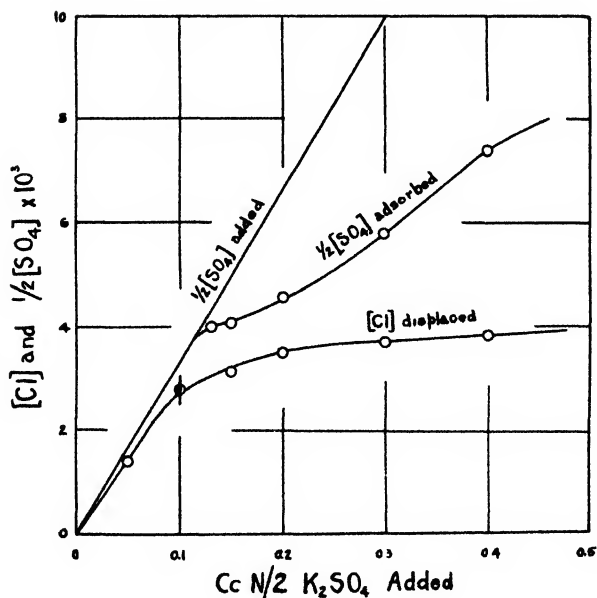


FIG. 9

Curves for the Simultaneous Displacement of Chloride and Adsorption of Sulfate by Colloidal Fe_2O_3 Sol.

TABLE IV

Adsorption of Sulfate by Cr_2O_3 Sol
(15.0 cc of sol with 0.5 N K_2SO_4)

K_2SO_4 0.5 N cc	SO_4 added mg	SO_4 in solution mg	SO_4 adsorbed mg	$\frac{1}{2} \text{SO}_4 $ adsorbed $\times 10^3$	$\frac{1}{2} \text{SO}_4 $ corrected $\times 10^3$	$\frac{1}{2} \text{SO}_4 $ added $\times 10^3$
0.30	7.20	0.10	7.10	9.67	9.86	10.00
0.35	8.40	0.34	8.06	10.94	11.19	11.67
0.40	9.60	0.88	8.72	11.80	12.11	13.33
0.50	12.00	2.31	9.69	13.03	13.42	16.67
0.60	14.40	3.95	10.45	13.96	14.52	20.00
0.70	16.80	4.88	11.92	15.82	16.56	23.33
0.80	19.20	6.00	13.20	17.41	18.33	26.67
0.90	21.60	7.90	13.70	17.95	19.02	30.00

Adsorption by Ferric Oxide. The adsorption data with ferric oxide sol are given in Table V and Fig. 9.

TABLE V

Adsorption of Sulfate by Fe_2O_3 Sol
(15.0 cc of Sol with 0.5 N K_2SO_4)

K_2SO_4 0.5 N cc	SO_4 added mg	SO_4 in solution mg	SO_4 adsorbed mg	$\frac{1}{2} \text{SO}_4 $ adsorbed $\times 10^3$	$\frac{1}{2} \text{SO}_4 $ corrected $\times 10^3$	$\frac{1}{2} \text{SO}_4 $ added $\times 10^3$
0.13	3.12	0.24	2.88	3.97	4.00	4.33
0.15	3.60	0.68	2.92	4.02	4.06	5.00
0.20	4.80	1.49	3.31	4.54	4.60	6.67
0.30	7.20	3.03	4.17	5.68	5.79	10.00
0.40	9.60	4.23	5.37	7.27	7.46	13.33
0.50	12.00	5.77	6.23	8.38	8.63	16.67

Conclusion

At all concentrations both above and below the precipitation value, sulfate ion enters into exchange adsorption with chloride ion present in the diffuse outer layer of the hydrous oxide particles. The sulfate adsorption curve follows a smooth course above that of the chloride displacement curve through the entire concentration range.

Summary

The following is a summary of the results of this investigation.

1. A comparison is made of the methods employed by Weiser and by Rabinowitsch for following the stepwise displacement of chloride ion from hydrous oxide sols during the dropwise addition of electrolyte to the sol.

2. The so-called superequivalent displacement of chloride observed by Rabinowitsch by his method of "rapid titration" is the result of an unsatisfactory experimental procedure which (a) produces localized coagulation of a portion of the sol below the precipitation value and (b) does not allow time for equilibrium to be approached.

3. The final equilibrium concentration of chloride following localized coagulation of the sol is higher than in the absence of coagulation since the coagulation process is not completely reversible in a reasonable time.

4. At all concentrations both above and below the precipitation value, sulfate ion enters into exchange adsorption with chloride ion present in the diffuse outer layer of the hydrous oxide particles.

5. Contrary to observations of Peterson and Storks on the adsorption of chromate by hydrous alumina both above and below the precipitation value, the sulfate adsorption curve follows a smooth course above that of the chloride displacement curve throughout the entire concentration range. The most marked break in the adsorption curve obtained by Peterson and Storks is probably due to a displacement of the adsorption equilibrium by ultrafiltration.

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STUDIES ON SILICIC ACID GELS

II. The Time of Set as a Function of the Temperature*

BY CHARLES B. HURD AND P. SCHUYLER MILLER

Introduction

In the preceding paper of this series of studies on the setting process of silicic acid gels¹ a series of determinations of the time of set as a function of the temperature was given. Aqueous solutions of one commercial brand of water glass were mixed with solutions of acetic acid at various temperatures. The time of set was determined by the tilted rod method.

It was pointed out in the article that if certain simple assumptions were possible, the time of set could be treated according to the ordinary laws for the velocity of a chemical reaction. By the use of Arrhenius' equation, a series of values for the heat of activation were obtained. The mean value, 16,940 calories, comes well within the limits for the heat of activation for ordinary reactions. The value was reasonably constant for various mixtures of solutions of the same water glass with acetic acid.

It was, of course, immediately apparent that a further study should be made of this phenomenon, in order to ascertain if the same value would be obtained with solutions of other samples of water glass and acetic acid. The next step would be to substitute other acids for the acetic acid. The third study should include the results where deliberate attempt had been made to modify the composition or structure of the original silicate.

The work reported in the previous paper was carried out with a water glass which can no longer be obtained. The silicates used in the work reported in the present paper and in the work now under investigation can be secured at any time, and their soda-silica ratio can be obtained from the maker, the Philadelphia Quartz Company.²

The present paper includes the results of a series of determinations on six brands of sodium silicate. Acetic acid only was used. The results appear interesting and will, we believe, assist somewhat in obtaining a useful picture of the process of setting of silicic acid gels.

Historical

As previously mentioned in this article, Hurd and Letteron have shown that it is possible, by means of certain simple assumptions, to treat the process of the setting of a silicic acid gel according to the laws for the velocity

* Contribution from the Chemical Laboratory of Union College, Schenectady, N.Y.

¹ C. B. Hurd and H. A. Letteron: *J. Phys. Chem.*, **36**, 604 (1932).

² The writers wish to acknowledge their gratitude to the Philadelphia Quartz Company for their courtesy in supplying not only all of the silicates used in these studies, but also for supplying analyses, methods of analysis, and other valuable information.

of ordinary chemical reactions. No other measurements of this kind have been found in the literature.

It has also been found, by a search of the literature, that little is known concerning the heat of setting of silicic acid gels. Thomsen¹ has reported that he found no heat effect during the coagulation of silicic acid; but his coagulation was slow, the time being at least 30 minutes, and he used dilute solutions. Graham² however, had reported about twenty years before that a rise of 1.1°C occurred during the setting of a 5% jelly. It does not appear possible to calculate the heat of formation from Graham's data. On the ordinary interpretations of 5%, however, the value of heat of setting would appear to lie between 1100 cal. and 2000 cal. per gram. mol. of H_2SiO_3 .

Wiedemann and Lüdeking³ attempted to determine the heat of setting of solutions of colloids by means of a calorimeter of about 18 cc. capacity. They accelerated the setting of a mixture of solutions of water glass and hydrochloric acid by means of ammonia. Their results appear consistent, but their values of $C = 12.2$ and 11.2 cal. are difficult to correlate to our present heats of reaction.

Experimental

We have determined the time of set for various mixtures of solutions of six different brands of sodium silicate with solutions of acetic acid at several different fixed temperatures. The silicate samples were supplied by the Philadelphia Quartz Company. The acetic acid from which the solutions were made was glacial acetic acid, C.P., J. T. Baker. All water used was freshly distilled water which was boiled in lots of 3 to 4 liters to expel all gases, especially carbon dioxide. After being boiled vigorously, it was cooled quickly in snow and was kept, as were all solutions, in tightly stoppered glass bottles.

The strength of all solutions was determined by titration. Silicate solutions were titrated for their alkali content with standard sulfuric acid, using methyl orange. The acetic acid solutions were titrated with standard sodium hydroxide, using phenolphthalein. The silica content was determined for the silicate solutions from the alkali content and the known soda-silica ratio supplied by the maker. We have checked this gravimetrically in one case. The silicate solutions were not filtered. Very little suspended matter was visible. A very slight sediment was noticeable after several weeks, although at the time the samples were used practically no deposit was visible.

Runs were made by mixing accurately measured volumes of the standardized dilute silicate solution, the standardized dilute acetic acid solution and distilled water. The solutions and the water had been standing for hours in tightly stoppered containers in an accurately controlled water thermostat. Two 100 cc. Pyrex Griffin beakers, carefully cleaned and dried, had stood for several minutes in the thermostat immersed to within 1 cm. of the top.

¹ J. Thomsen: "Thermochemische Untersuchungen," 1, 211 (1882).

² T. Graham: J. Chem. Soc., 17, 318 (1864).

³ E. Wiedemann and C. Lüdeking: Ann. Physik, (3) 25, 145 (1885).

They had been covered with watch glasses. The measured volume of dilute solution was placed in one, and the measured volume of dilute acetic acid in the other. The water was added to the acid. At a given time the silicate was quickly poured into the acetic acid with stirring. To avoid the loss of the silicate solution which adheres to the beaker, the same beaker had had the same amount of silicate poured from it a few minutes before. We found this method necessary and accurate. The possible error in the volume of the silicate solution was found to be negligible. This rapid mixing avoided errors in the timing, especially for short runs.

The beaker containing the resulting mixture was covered with a watch glass and placed on a tray in the thermostat, immersed in the water so that the level of water on the outside was higher than that of the solution inside. The beakers with watch glass covers just failed to float. The volume in the beaker was always 80 cc., except in the case of the 0° thermostat, where a different procedure proved necessary.

The contents of a number of beakers in the thermostat were watched until the peculiar opalescent appearance preceding setting was observed. The stirring rod test for setting was then applied. This has been described in the preceding paper. It is carried out as follows. A stirring rod 10 cm. in length and made of glass 3 mm. in diameter is drawn out to a short stubby point, the tapered portion being about 5 mm. long. The point is fire polished. The rod is thrust into the gel at an angle of about 20° to the vertical. The gel is considered set when the rod fails to fall over. An operator with a little experience can obtain check determination differing by less than 2% of the time easily and regularly. Two different operators can check each other. A deliberate attempt to mutilate the surface and body of the gel will not produce errors greater than 3%. The beakers are not removed from the bath during testing.

Four thermostats were used. In the 0° thermostat, the mixtures for which the time of set was to be determined were contained in 200 cc. Erlenmeyer flasks. These were corked and 100 cc. beakers were inverted over the cork to prevent water leaking inside. They were buried in damp fine snow. The snow was frequently replenished from above. The excess water produced was withdrawn from below. Tests showed that the contents of the flasks remained within .1° of 0° C. A longer rod of the same diameter was used to determine the time of set. This method proved much simpler for the operator at 0° C. than the method of keeping the mixed solutions, 80 cc. in volume, in 100 cc. beakers as was done at other temperatures. The method of burying the 160 cc. mixtures in flasks in the snow was not adopted, however, until careful tests showed that the same results were obtained with the easier method than with the method of beakers at the same temperature. The method of burying the flasks guaranteed much closer thermal control.

The three other thermostats were made out of metal tubs about 20 inches in diameter and 12 inches deep. The 26° bath had no external insulation but those at 40° and 56° were insulated by a layer of dry sawdust

between the tub and a much larger tub. Each was stirred by a brass paddle stirrer. The temperatures of the 26°, 40° and 56° baths were controlled by toluene mercury regulators.

The 26° bath had a 100 watt intermittent heater controlled through a relay by the regulator. The 40° bath had a Cenco 125 watt continuous heater of the knife type and a 125 watt intermittent heater controlled by the regulator and a relay. To reduce arcing at the relay contacts a 15 watt carbon lamp was connected across the relay contacts. The 125 watt heater was, therefore, controlled by the regulator in that the relay simply shunted from time to time, as necessary, the 15 watt lamp in series. Using this scheme, no arcing even with 250 watt heaters has been observed and the telephone relays, Western Electric E 493, have worked satisfactorily. The 56° bath had one 250 watt continuous heater and a 250 watt heater controlled as in the case of the 40° bath. We have not found temperature variation as large as .1°C during any of our runs.

Timing was accomplished by means of a stopwatch or a good ordinary watch for the longer runs. The temperature of the thermostat was checked frequently. The watch glasses fitted tightly and, apparently, during the setting, a negligible amount of water or acetic acid was lost through evaporation. Containers in which gel had set were washed carefully with dilute sodium hydroxide and thoroughly with water, although tests had shown no measurable effect on the time of set through the presence of particles of a previously set gel.

In all of the runs reported here, we have kept the silica concentration constant. Because of the different soda-silica ratios of the samples, this has meant a different sodium hydroxide concentration with different samples. For any one brand of silicate, however, the sodium hydroxide concentration was constant, as was, of course, the silica concentration. Six different concentrations of acetic acid were used.

The results obtained are given in the following tables. Trouble was experienced in the case of the "B.W." brand of water glass. Here the high soda concentration necessitated the highest concentration of acetic acid. It was found that when the silicate was poured into the acetic acid-water mixture the result curdled somewhat except at 0°. This caused an error which is readily observed in the tables.

In the results which follow the average of the time for at least two satisfactory runs is given for each mixture at each temperature. Ordinarily three check runs were made. An immense amount of work was required. Each table gives the soda-silica ratio, the concentration in the resulting mixture, expressed in gram mols per liter and the time of set in minutes for four different temperatures expressed in degrees Centigrade. It should be noted that the soda-silica ratio as given is a weight ratio. The mol. ratio is 1.032 times the weight ratio; for example the weight ratio of the C brand is given by the maker as 1:2.00, giving 1:2.06 for the mol ratio.

Tables showing Time of Set for Various Mixtures

TABLE I

"S" brand Water Glass
Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.86$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	26.2°	40.7°	55.8°
0	.323	.644	.500	1308.	89.	24.0	7.0
1	"	"	.625	2001.	134.	39.5	11.0
2	"	"	.750	2715.	177.	53.3	14.0
3	"	"	.875	3242.	224.	66.0	18.0
4	"	"	1.000	3807.	265.	74.0	21.8
5	"	"	1.125	4502.	308.	86.0	25.0

TABLE II

"N" brand Water Glass
Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.22$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	28.0°	40.6°	55.8°
0	.388	.646	.625	1440.	87.	26.5	8.4
1	"	"	.750	1990.	121.	39.8	11.1
2	"	"	.875	2787.	160.	53.0	16.4
3	"	"	1.000	3550.	196.	62.5	20.5
4	"	"	1.125	3891.	218.	74.0	23.2
5	"	"	1.250	4700.	260.	84.0	26.8

TABLE III

"K" brand Water Glass
Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.84$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	27.4°	40.4°	56.2°
0	.440	.646	.625	1080.	66.0	19.7	5.9
1	"	"	.750	1648.	97.0	29.2	9.1
2	"	"	.875	2214.	133.0	41.3	11.8
3	"	"	1.000	2789.	166.0	53.0	15.0
4	"	"	1.125	3108.	201.0	63.0	18.0
5	"	"	1.250	3518.	233.0	68.7	19.4

TABLE IV

"U" brand Water Glass
Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.44$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	25.9°	40.4°	55.8°
0	.508	.640	.750	1568.	105.5	26.2	8.3
1	"	"	.875	2118.	145.0	38.7	11.2
2	"	"	1.000	2720.	189.0	50.5	14.4
3	"	"	1.125	3264.	228.0	60.5	18.3
4	"	"	1.250	3585.	265.0	70.5	20.7
5	"	"	1.375	4092.	292.0	81.7	24.4

TABLE V
 'C' brand Water Glass
 Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.00$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	25.9°	40.4°	55.8°
0	.623	.642	.750	560.	38.0	10.3	3.1
1	"	"	.875	1063.	73.7	20.9	5.6
2	"	"	1.000	1568	108.0	29.8	8.5
3	"	"	1.125	1972.	142.0	38.2	10.6
4	"	"	1.250	2375.	165.0	48.0	13.2
5	"	"	1.375	3113.	199.0	55.5	16.1

TABLE VI
 "B.W." brand Water Glass
 Ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:1.58$

Mixture	Concentrations			Time of Set—Minutes			
	NaOH	SiO_2	CH_3COOH	0.0°	26.3°	40.3°	55.8°
0	.791	.645	.938	255.	20.9	5.0	1.8
1	"	"	1.091	730.	52.0	13.6	3.9
2	"	"	1.250	1076.	76.5	20.4	6.4
3	"	"	1.408	1340.	100.0	28.5	8.1
4	"	"	1.561	1570.	123.0	32.6	9.8
5	"	"	1.720	1900.	142.0	40.0	11.4

For each brand of silicate the logarithm of the time of set given in Tables I to VI for each of the six mixtures was obtained. This was plotted as ordinate against the reciprocal of the absolute temperature as abscissa. A typical set of curves for the "C" brand is shown in Fig. 1. From the curves for the six mixtures of each brand of silicate, the slope was obtained. The curves were found to be linear. These values are tabulated in the following table:

TABLE VII
 Values for the Slope of the Curves for Log Time of Set against
 Reciprocal Absolute Temperature

Mixture	Brand "S"	"N"	"K"	"U"	"C"	"B.W."
		(Values in degrees)				
0	3668.	3640.	3638.	3662.	3660.	3512.
1	3632.	3625.	3690.	3675.	3644.	3616.
2	3673.	3600.	3607.	3666.	3648.	3582.
3	3667.	3618.	3625.	3666.	3635.	3593.
4	3628.	3581.	3620.	3600.	3628.	3584.
5	3601.	3569.	3608.	3572.	3628.	3600.

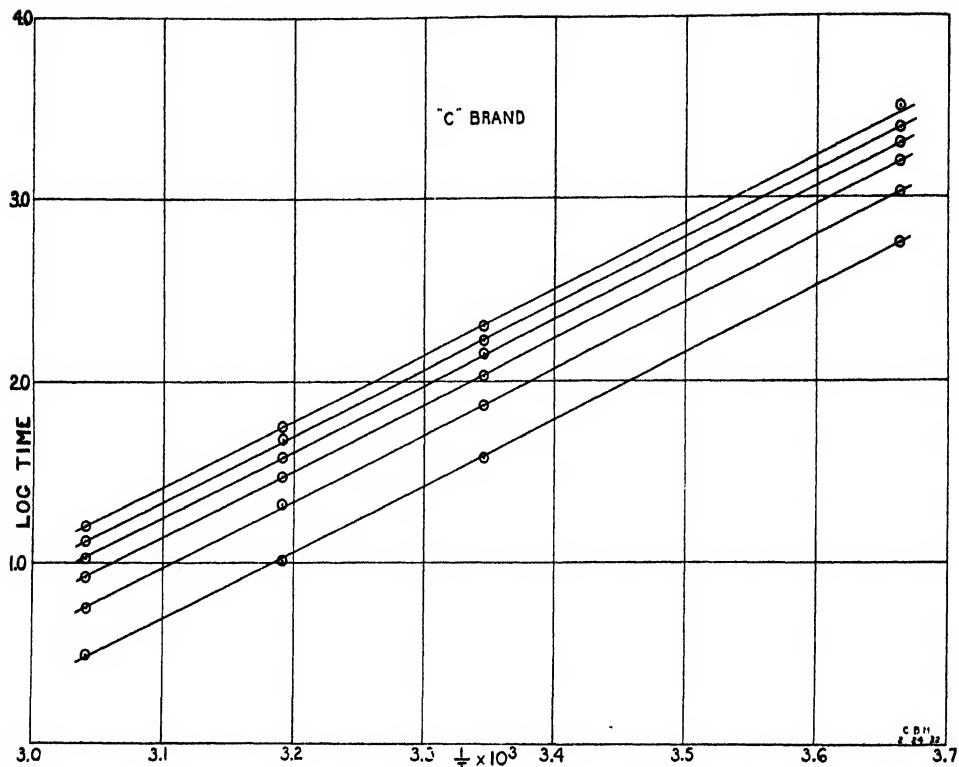


FIG. 1
Effect of Temperature on Time of Set.

The values are seen to show good agreement except for the "B.W." brand. The mixtures for this silicate, except those at 0° , showed curdling, as has been mentioned. Their lack of agreement is, therefore, to be expected. The curdling was more pronounced, the higher the temperature. It seems reasonable to assume that where curdling occurred, the concentration of reacting substances in the solution would be decreased. This would result in a slower reaction and a larger value of log time of set at higher temperatures. This would flatten the $\log t'$ against $1/T$ curves and would give smaller values for the slope. This agrees with the results in Table VII for the "B.W." brand.

Interpretation of Results

As one of us has suggested in a previous paper,¹ we may make certain assumptions in our interpretation of these results. These assumptions are not unreasonable, and they lead to interesting results. They are:

1. That we are dealing with a process which follows the laws of ordinary chemical reactions so far as its velocity is concerned.
2. That Arrhenius' equation may be applied to our results.

¹ C. B. Hurd and H. A. Letteron: J. Phys. Chem., **36**, 604 (1932).

3. That for a given run the time of set measures the time when a certain fixed proportion of the silica, in whatever form, has reacted.

These assumptions are discussed in the paper to which reference has been made. If we develop our ordinary equations for the velocity of a chemical reaction where

x = amount changed in time, t

a = original concentration

n = order of reaction

we shall obtain the following familiar equations:

$$\frac{dx}{dt} = k(a-x)^n \quad (1)$$

$$\frac{dx}{(a-x)^n} = k dt \quad (2)$$

gives
$$\frac{1}{n-1} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] = kt \quad (3)$$

It is easily shown for any fractional change of the concentration a , that the time, t' is given by the relation

$$t' = \frac{c'}{ka^{n-1}} \quad (4)$$

where c' = constant depending upon fraction x/a and on n .

We may now write Arrhenius' equation

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{d \ln k}{d 1/T} = - \frac{Q}{R} \quad (5)$$

From (4) we obtain

$$\ln t' = \ln c' - \ln k - (n-1) \ln a \quad (6)$$

If now we maintain a and x/a constant, we may obtain from (5) and (6)

$$\ln t' = + \frac{Q}{RT} - (n-1) \ln a + c'' \quad (7)$$

From our values of Table VII, obtained as the slope of the curves for $\log t'$ against $1/T$ illustrated by Fig. 1, we may obtain values for the heat of activation, Q , for the setting process for gels from the six brands of water glass. They are obtained by multiplying the values given in Table VII by 2.303 R , since by equation (7)

$$\frac{d \ln t'}{d 1/T} = \frac{Q}{R} \quad \text{Table VIII gives the results.}$$

TABLE VIII

Values of the "Heat of Activation" for the Setting of Silicic Acid Gels

	"S"	"N"	"K"	"U"	"C"	"B.W."
0	16795	16667	16657	16767	16757	16080
1	16630	16595	16895	16826	16684	16555
2	16815	16483	16515	16786	16702	16401
3	16790	16952	16595	16786	16643	16451
4	16612	16395	16575	16483	16612	16410
5	16505	16342	16520	16350	16612	16482
mean	16691	16572	16626	16666	16668	16397

These figures show remarkable agreement. An estimate of the possible error from the accuracy of the timing and temperature measurements, considering that in all cases the logarithm of time plotted was the mean of at least two separate determinations, gives as the maximum probable error in the value of the "heat of activation" less than 2%.

It is noticeable, however, that the six values for each brand, going downward in each vertical column in Table VIII, show a drift toward lower values. That is, a general decrease in the heat of activation is shown for each brand as the acidity of the mixtures increases. This decrease is not large, but since it occurs in each of the five columns, it is apparently not the result of error. We should note at this point, of course, that it is more difficult to thermostat a 250 cc. Erlenmeyer flask and its contents for three days at 0° than it is to keep the contents of a beaker at 26° for three hours, but errors in the ice bath readings alone could not alter the slope of the curves. They are the result of points obtained from data at all four temperatures.

Formulation of a Theory. It is difficult to formulate a theory which shall give a clear picture of the process of setting of a silicic acid gel and which shall, of course, be subject to verification or rejection on the basis of experimental results. As has been pointed out in the preceding paper, the lack of sufficient quantitative data constitutes a real difficulty. From a study of existing data, however, and a consideration of certain of our own experimental results, a part of which are as yet unpublished, we are prepared to suggest the following theory for examination.

When a solution of sodium silicate and a dilute acid are mixed, a practically instantaneous reaction occurs, forming silicic acid and the sodium salt of the acid used, the latter, of course, mainly in the ionized form. The silicic acid particles slowly coalesce to form a structural framework for the gel. Beyond a certain stage, this process proceeds rapidly. The mechanism of linkage appears to be that of the splitting out of water from two hydroxyl groups of neighboring molecules of silicic acid. This agglomeration continues until the whole mass is filled with a fibrillar framework.

There is, in the literature, sufficient evidence to convince us that the exclusion of the solid-solution theory supported by Katz¹ and the emulsion

¹ Katz: *Kolloidchem. Beihefte*, 9, 1 (1918).

theory, supported by Wo. Ostwald¹ is justified. Certain work under investigation in this laboratory, on the electrical conductivity of mixtures of sodium silicate and acetic acid during the process of setting, cause us to favor the fibrillar or brush-heap theory rather than the cellular theory.

It is impossible to give any definite reference for the genesis of the idea of the splitting out of water molecules from hydroxyl groups of neighboring molecules of silicic acid. It is a common idea to be found in both organic and inorganic chemistry. Compare the discussion on the polysilicic acids in Mellor.² The formation of higher silicic acids, in connection with silicic acid gels has been mentioned by Jordis³ while the idea of chains held together by chemical forces in the silicic acid gel was stated by Gaunt and Usher.⁴ They have even postulated a long, highly hydrated chain to give the ratio of meta-silicic acid. The linkage is through oxygen atoms.

A similar idea in the organic field has been suggested by Kienle⁵ in a theory for the formation of artificial resins. It should be noted that in this case the condensation takes place between hydroxyl groups on molecules of different substances, such as glycerine and phthalic acid.

We had believed, when starting this research, that a difference might be found in the time of set and in the effect of temperature on the time of set if the composition of the original sodium silicate could be varied considerably. This we have done, varying the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio from 1:3.86 in the "S" brand which gives a mol ratio of 1:3.99 or essentially 1:4., down to a mol ratio of 1:1.63 for the "B.W." brand. If the process of gel formation requires the formation of chains of partially dehydrated silicic acid, formed by the splitting out of molecules of water from neighboring hydroxyl groups, it is evident that in a solution in which the process has already partially occurred, such as a solution containing trisilicic acid, the gel formation should occur more rapidly than in a solution containing ortho or metasilicic acid. It is conceivable though not necessarily probable, that the effect of temperature on the rate of reaction should be different.

It is, of course, not at all certain that we have in the solution of the "S" brand, let us say, any different form of silicic acid than we have in the solution of any of the others, although one might expect to find sodium salts of the higher silicic acids in those samples of silicate where the ratio of the number of mols of silica to one of soda is high, such as the "S" brand with the mol ratio $\text{Na}_2\text{O}:\text{SiO}_2$ of 1:3.99.

It has been shown in various studies of aqueous solutions of sodium silicates, such as the work of Kahlenberg and Lincoln⁶ on the lowering of the freezing point and the electrical conductivity of solutions of sodium meta-

¹ Wo. Ostwald: "Theoretical and Applied Colloid Chemistry," translated by Fischer, 103 (1917).

² J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 6, 308 (1925).

³ E. Jordis: *Z. anorg. Chem.*, **44**, 200 (1905).

⁴ Gaunt and Usher: *Trans. Faraday Soc.*, **24**, 32 (1928).

⁵ R. Kienle: *Ind. Eng. Chem.*, **22**, 590 (1930).

⁶ L. Kahlenberg and A. T. Lincoln: *J. Phys. Chem.*, **2**, 77 (1898).

silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, that the experimental evidence shows the influence of 2 Na and 2 OH ions but shows no evidence of a SiO_3 ion. This hydrolysis had been mentioned previously by Kohlrausch. On the other hand, Harman¹ presents evidence to show the existence of the SiO_3 anion in solutions of silicates of low soda-silica ratio, such as 1:1, but he states that in solutions of high ratio such as 1:3 or 1:4 the simple SiO_3 ion is not present, but there are present either aggregations of simple silicate ions with or without colloidal silica or definite complex silicate ions.

We feel, therefore, unable to state with certainty that we are starting our reaction with silicic acid in different form, from the "S" brand down to the "C" brand. Our results show, however, that the effect of temperature on the time of set is the same, from the "S" to the "C" ratios in acid solutions, as is shown by the values given in Table VIII.

It would be very interesting to discover whether the actual time of set is affected by the original soda-silica ratio, in two solutions having the same final sodium hydroxide, silica and acetic acid concentrations, one of which was produced by adding acetic acid to a low soda-silica ratio silicate such as the "C" brand with its ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.06$ mol ratio while the other was made by adding sodium acetate and acetic acid to a solution of a silicate such as the "S" brand with a soda-silica ratio 1:4, mol ratio. We cannot answer this question from the results given in this paper, but the results of a series of determinations of this type at present under way in this laboratory should answer the question as to whether the original condition of the silica affects the time of set.

A comparison of the values of the "heat of activation," mentioned in this paper, the average being $Q = 16,640$ calories with the average value obtained in the previous paper by Hurd and Letteron, $Q = 16,940$ calories, confirms the results given in that paper with much greater accuracy.

Summary

The time of set of various mixtures of solutions of six different commercial sodium silicates with acetic acid at four different temperatures have been determined. The soda-silica ratios range from 1:4.0 to 1:1.63 mol ratio. The temperatures were approximately 0° , 26° , 40° and 56°C .

The effect of temperature on time of set was found to be the same, regardless of the soda-silica ratio. A value was obtained for a quantity analogous to Arrhenius' heat of activation for a homogeneous chemical reaction. The average value of 16,640 calories was obtained. The data given here confirm the former results, obtained by Hurd and Letteron, on various mixtures of one sample of sodium silicate with acetic acid.

A theory for the mechanism of formation of a silicic acid gel has been suggested.

The theory has been considered from the point of view of the effect of the temperature on the time of set.

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¹ R. Harman: *J. Phys. Chem.*, **29**, 1155 (1925); and more especially **30**, 359 (1926).

PHOTOCHEMICAL REDUCTION OF CARBON DIOXIDE IN AQUEOUS SOLUTION

BY M. QURESHI AND S. S. MOHAMMAD

Since the advent of the formaldehyde theory of photosynthesis, suggested by M. Berthelot in 1860 and formulated clearly by Baeyer in 1870, a number of attempts have been made by different workers to reduce carbon dioxide with the help of light-energy in the laboratory. The ordinary 'dark' reaction, involving the reduction of carbonic acid to formic acid by means of nascent hydrogen in the presence of alkalis, discovered by Kolbe and Schmidt¹ and confirmed by Malay² and Ballo,³ was shown by Lieben⁴ to be unaffected by light. Fenton⁵ was able to accomplish the reduction of CO₂ in aqueous solution direct to formaldehyde without the intermediate formation of formic acid, by means of metallic magnesium. There is nothing in the literature, as far as the writers are aware, to prove that this reaction is influenced by light.⁶ Losanitsch and Jovitschitsch,⁷ and Löb⁸ tried the effect of silent electric discharge, which may be regarded as equivalent to that of the short wave ultra-violet light, on the system, CO₂ + water vapour, and found formic acid and formaldehyde, among the products of the reaction.

D. Berthelot and Gaudechon,⁹ using ultra-violet light from a quartz mercury lamp, succeeded in obtaining formaldehyde from mixtures of carbon dioxide and hydrogen, and CO and hydrogen, but failed to obtain formaldehyde from CO₂ and water. Stoklasa and Zdobnický¹⁰ found that CO₂ was reduced to formic acid by nascent hydrogen in the presence of potassium hydroxide. When ultra-violet light was used and other conditions remained the same, formaldehyde and sugar were formed. No formaldehyde was obtained by the action of ultra-violet on CO₂ and water, unless nascent hydrogen and potassium hydroxide were also present. Contrary to this, Usher and Priestley¹¹ and Baly, Heilbron and Barker¹² claimed to have got formaldehyde by exposing aqueous solutions of CO₂ to ultra-violet light. Spoehr,¹³ Baur and

¹ Ann., 119, 251.

² Ann., 135, 118.

³ Ber., 6 (1884).

⁴ Monatshefte, 1895-1897.

⁵ J. Chem. Soc., 1907, 687.

⁶ Quantitative experiments carried out in this laboratory show that the reaction is not influenced by light. Dhar has, however, recently reported to the contrary in 'Nature' of Feb. 6, 1932.

⁷ Ber., 30, 135 (1897).

⁸ Z. Elektrochemie, 1906, 1174.

⁹ Compt. rend., 150, 1690 (1910).

¹⁰ Biochem. Z., 30, 432 (1911).

¹¹ Proc. Roy. Soc., 84B, 101 (1911).

¹² J. Chem. Soc., 119, 1025 (1921).

¹³ J. Am. Chem. Soc., 45, 1184 (1923).

Rebmann,¹ Baur and Büchi,² and Porter and Ramsperger³ on repeating the work of the above-mentioned authors failed to obtain any trace of formaldehyde or sugars. The work of Porter and Ramsperger proved the importance of exercising extreme care in avoiding contamination of materials with organic matter in experiments of this nature. Positive tests for formaldehyde were invariably obtained whenever CO₂ came in contact with wax or grease; whereas negative tests were obtained when the joints were replaced by quartz-to-glass seals. Baly and collaborators⁴ in a later paper claimed to have obtained complex compounds of the nature of carbohydrates by exposing aqueous solutions of CO₂, in which white insoluble powders, capable of adsorbing carbonic acid were suspended, to the action of ultra-violet light. Aluminium powder, barium sulphate, freshly precipitated aluminium hydroxide and the basic carbonates of aluminium, magnesium and zinc were employed. Mezzadrolì and co-workers⁵ obtained formaldehyde and small quantities of sugar by exposing solutions of bicarbonates of different metals to ultra-violet light.

Attempts were also made by many workers to reduce CO₂ in the visible light or sunlight in the presence of various inorganic and organic catalysts. Moore and Webster⁶ claimed to have effected the synthesis of formaldehyde from CO₂ and water in sunlight by employing various inorganic catalysts such as uranyl salts, colloidal ferric hydroxide, etc. Baly and Heilbron⁷ also obtained formaldehyde by exposing solutions of CO₂ to visible light in the presence of chlorophyll, malachite green, and methyl orange. Spoehr, Baur and Rebmann and Baur and Büchi, in the works already cited, failed to confirm the results of the above-mentioned authors. The whole subject of photosynthesis *in vitro* received a fresh stimulus through the publication of a series of papers by Baly and his collaborators,⁸ in which the authors claimed to have obtained carbohydrates through the reduction of carbonic acid adsorbed on the surface of coloured powders in the visible light. The powders employed were freshly prepared pure basic carbonates of nickel, and cobalt. On passing CO₂ through conductivity water containing the above powders in suspension, and exposing it to the light of an ordinary tungsten lamp or a 100 watts half-watt lamp, deductable quantities of organic matter, were obtained within two hours. The photosynthesis of organic matter ceased after two hours, owing to the poisoning of the surface of the catalyst, and greater intensity of illumination led to the decomposition of carbohydrates already formed. In later experiments, nickel carbonate, prepared electrolytically and activated by exposure to white light for six hours, was used.⁹ Recently Baly¹⁰ has described

¹ *Helv. Chim. Acta*, **5**, 828 (1922).

² *Helv. Chim. Acta*, **6**, 959 (1923).

³ *J. Am. Chem. Soc.*, **47**, 79 (1925).

⁴ *Proc. Roy. Soc.*, **116A**, 197 (1927).

⁵ *Atti Accad. Lincei*, (6) **6**, 160 (1927).

⁶ *Proc. Roy. Soc.*, **87B**, 163 (1913).

⁷ *J. Soc. Chem. Ind.*, **40**, 377R (1921).

⁸ *Proc. Roy. Soc.*, **116A**, 212, 219 (1927).

⁹ *Proc. Roy. Soc.*, **122A**, 393 (1929).

¹⁰ *Trans. Faraday Soc.*, **27**, 545 (1931).

another series of experiments, in which nickel carbonate, ferric oxide, and chromium oxide, supported on aluminated Kieselguhr, were found to be efficient in the photosynthesis of carbohydrates. It is claimed that with such supported catalysts, 0.0025 grms of organic matter can be synthesized per one gram of the powder used in two hours. Bell,¹ on repeating the work of Baly and collaborators, fails to obtain any indication of photosynthesis.

Dhar and Sanyal,² employing direct sunlight, claimed to have obtained formaldehyde from aqueous solutions of CO₂ alone and in the presence of inorganic and organic 'photo-catalysts,' such as ferric chloride, colloidal ferric hydroxide, copper sulphate uranyl nitrate, chromium sulphate, methylene blue and methyl orange. This was, however, contradicted by Burk,³ who failed to obtain a positive test for formaldehyde, by making use of pure reagents and concentrated sunlight. In view of the objections raised by Burk, G. Rao and Dhar⁴ repeated the experiments of Dhar and Sanyal, with some additions, and still obtained positive tests for formaldehyde and in some cases for carbohydrates. Recently, Atma Ram and Dhar⁵ have published another paper, dealing with the same subject in which a great variety of coloured catalysts including those already used, has been employed. It is claimed that aqueous solutions of sodium bicarbonate mixed with some of these coloured catalysts and exposed to direct sunlight in sealed glass bulbs for many hours give positive tests for formaldehyde and carbohydrates.

The above review of the literature on the subject of photosynthesis *in vitro*, while showing the contradictory nature of results obtained by various workers in this important field of research, indicates the necessity of repeating the work already done and exploring fresh avenues of attack on the problem. The following is the first instalment of the work that is being conducted in this laboratory in this connection.

Experimental

The experiments detailed below were performed with three different sources of light, namely quartz mercury vapour lamp, direct sunlight, and tungsten filament lamps. All the chemicals employed were either Kahlbaum's special reagents or Merck's extra pure chemicals. In certain doubtful cases, they were prepared freshly in the laboratory or purified by recrystallisation. In many cases, two control experiments, one with simple water to guard against the contamination of CO₂ and another without CO₂ to test the action of light on the substance employed as a catalyst were performed. The water used for the preparation of solutions and for the purposes of tests was twice-distilled conductivity water. The carbon dioxide gas, employed in these experiments, was obtained by the action of pure hydrochloric acid on marble and passed through four wash bottles, containing chromic acid, sulphuric acid, and conductivity water, before use. When grease is not employed on the

¹ Trans. Faraday Soc., **27**, 771 (1931).

² J. Phys. Chem., **29**, 926 (1925).

³ J. Phys. Chem., **31**, 1338 (1927).

⁴ J. Phys. Chem., **35**, 1418 (1931).

⁵ J. Phys. Chem., **36**, 567 (1932).

joints of the apparatus, simple washing of the gas with conductivity water is quite enough. The tests employed were as follows: Schryver's test for formaldehyde; Schiff's reagents (modified by Denige) for aldehydes in general; Tollens' reagent, reduction of mercuric acid and permanganate of potash for formic acid; Molisch test for carbohydrates; Fehling's solution for reducing sugars and formaldehyde; Benedict's solution for reducing sugars only. Since a large portion of these experiments depend for their reliability on the purity of materials used and the care taken in the application of Schryver's test, it was thought necessary to find out by preliminary examination, the degree of sensitiveness and the optimum conditions for the successful application of the test. Examination with known solutions of formaldehyde of varying strength showed that this test is capable of detecting easily one part formaldehyde in 10^6 to 10^7 parts water. Even at this low concentration a clear pink colour develops within one second of the addition of the reagents, provided (1) the reagents are freshly prepared and (2) the amount of hydrochloric acid added is not below a certain limit. If the reagents are not freshly prepared the time required for the development of the colour increases. The amount of hydrochloric acid most suitable for the immediate development of the colour was found by taking 10 cc. of a solution of formaldehyde (1 in 10^6) and noting the time required for the appearance of pink colour after adding 2 cc of a 1% freshly prepared solution of phenylhydrazine hydrochloride, 1 cc of a 5% freshly prepared solution of potassium ferricyanide and varying amounts of hydrochloric acid (sp. gr. 1.126). The results tabulated in Table I show that the time decreases with increasing amount of hydrochloric acid, reaches a minimum with 3 cc of the acid, and then becomes constant with further increase in the amount of the acid.

TABLE I

Amount of HCl. (sp. gr. 1.126) added to 10 cc of the solution	Time required for the appearance of the pink coloration
1. 2 drops of HCl.	8 seconds
2. 4 " " "	5 "
3. 0.5 cc " "	3 "
4. 1.0 " " "	2.5 "
5. 2.0 " " "	1.5 "
6. 2.5 " " "	1.2 "
7. 3.0 " " "	within one second
8. 3.5 " " "	" " "
9. 4.0 " " "	" " "
10. 5.0 " " "	" " "

The pink colour changes into muddy red and then into purple after a few hours. It may be pointed out that simple conductivity water also develops a slight purple colour after 24 hours.

(a) *Experiments in Ultra-Violet Light.*

(1) A medium-sized flask of fused transparent quartz, containing conductivity water was placed at a distance of 6 inches from a quartz mercury vapour lamp of horizontal type, burning at 230 volts, 3.5 amps, and a fairly rapid stream of CO_2 was passed through it. The lamp was provided with a reflector at its back. The gas after bubbling through the illuminated water passed on to another flask, containing conductivity water, which was shielded from light. No positive test for formaldehyde or sugar was obtained with any of the two solutions after exposures extending from 2 to 24 hours.

(2) A vertical quartz mercury lamp of the immersion type (110 volts, 3.5 amps), manufactured by Hanovia Company was surrounded by a quartz jacket, through which water was kept running. The lamp, together with the jacket, was placed in a quartz beaker containing conductivity water, the latter being surrounded by a cylindrical vessel of copper, nickel-plated from inside. The lamp was started and kept running for periods of time varying from one to 24 hours, while a continuous stream of CO_2 was passing through the conductivity water. As before, no formaldehyde or carbohydrates could be detected. Experiments were repeated with barium sulphate and aluminium bicarbonate, suspended in conductivity water, but without success.

(3) Next monochromatic ultra-violet light was tried. The mercury lines 254 and 313 $\text{m}\mu$ were isolated by the following filters and filter combinations.

254 $\text{m}\mu$	Chlorine gas at 1 atm. pressure in a vessel of fused transparent silica with plane paralleled sides—thickness 4 cm.
313 $\text{m}\mu$	(1) Potassium chromate 0.2034 grm per litre
	(2) p-nitroso-dimethylaniline 0.014 grm per litre in two separate quartz cells 0.5 cm. each.

Carbon dioxide was passed through conductivity water placed in a small quartz flask placed immediately behind the filters. Exposures up to 32 hours failed to reveal any trace of formaldehyde.

(b) *Experiments in Sunlight.*

Two series of experiments were performed in direct sunlight; and in view of the repeated claims made by Dhar and collaborators,¹ many inorganic and organic catalysts employed by these authors, were used. In the first series of experiments, a fairly rapid stream of CO was passed through the solutions or suspensions, contained in flasks of pyrex placed in direct sunlight. In another closed flask, containing the same amount of materials and exposed for the same length of time, side by side with the first, no CO was passed. At the end of each experiment solutions were filtered and distilled under reduced pressure. The distillate was tested for formaldehyde, while the residue in the flask, after being evaporated to dryness and extracted with pure methyl alcohol, was

¹ Dhar and collaborators: J. Phys. Chem., 29, 926 (1925); 35, 1418 (1931); 36, 567 (1932).

examined for the carbohydrates. When formaldehyde was detected, it was estimated colorimetrically with the help of a colorimeter of a Duboscq type, made by the Klett Manufacturing Company. The results are tabulated in Table II.

TABLE II

System exposed	Time of exposure	Formaldehyde or carbohydrate detected	Estimated amount
1. Conductivity Water + CO ₂	4,6,12	none	
2. Conductivity Water + CO ₂ + Copper Sulphate	4,6	"	
3. Conductivity Water + CO ₂ + Ferric Chloride	4,6	"	
4. Conductivity Water + CO ₂ + Basic Nickel Carbonate	2,4,6	"	
5. Conductivity Water + CO ₂ + Basic Cobalt Carbonate	2,4,6	"	
6. Conductivity Water + CO ₂ + Chromium Sulphate	4,6	"	
7. Conductivity Water + CO ₂ + Manganous Chloride	4,6	"	
8. Conductivity Water + CO ₂ + Methyl Orange	4	Formaldehyde	0.0002%
9. Conductivity Water + Methyl Orange	4	"	nearly the same
10. Conductivity Water + CO ₂ + Malachite Green	4	"	0.00012%
11. Conductivity Water + Malachite Green	4	"	nearly the same
12. Conductivity Water + CO ₂ + Colloidal Chlorophyll	6	"	0.0001%
13. Conductivity Water + Colloidal Chlorophyll	6	"	nearly the same

In the second series of experiments, 100 cc of solutions were sealed in bulbs blown from ordinary glass and exposed to direct sunlight, usually between 10 in the morning and 4 in the afternoon. Tests were carried out as described above. The results are given in Table III.

TABLE III

System exposed	Time in hours	Formaldehyde or Carbohydrate	Estimated amount %
1. Conductivity water saturated with CO ₂	65	none	
2. 5% Solution of sodium hydroxide saturated with CO ₂	50	"	
3. 5% Solution of NaOH	50	"	
4. 5% Solution of sodium bicarbonate (Merck's)	50	Formaldehyde	0.0002
5. 5% Solution of sodium bicarbonate prepared in the laboratory	"	none	
6. 3% Sodium bicarbonate (Merck) 1 gm basic NiCO ₃	"	Formaldehyde	0.00018
7. Conductivity water (freshly boiled) + basic NiCO ₃ (1 gm) sealed after evacuation	65	none	
8. Water + NiCO ₃ + Impurities	55	Formaldehyde	0.0002
9. Conductivity water (freshly boiled) + copper acetate (1 gm) sealed after evacuation	55	Formaldehyde	0.0005
10. Colloidal Chlorophyll (0.0048 gm per 100 cc) sealed after evacuation	19 completely decolorized	"	0.0001

(c) *Experiments in the Light of a Tungsten Filament Lamp.*

These experiments were performed with finely powdered basic carbonates of nickel and cobalt purified according to the method described by Baly and collaborators in one of their papers, on "the photosynthesis of naturally occurring compounds."¹ The carbonates after being washed free from alkali were dried at 100° and activated by exposure to the light of a quartz mercury lamp for 30 minutes. Ten grams of these powders were suspended in 250 cc of conductivity water in a pyrex flask through which was maintained a continuous stream of CO₂. The flask was placed at a distance of 9 inches from a 500 watt tungsten filament lamp. After two hours exposure the contents of the flask were filtered and distilled under reduced pressure. The distillate was tested for formaldehyde while the residue in the flask, after being evaporated to dryness and extracted with pure methyl alcohol, was tested for carbohydrates. Experiments were repeated with increasing distances from the light source but no organic matter of the nature of carbohydrates was detected in the residue obtained after the evaporation of alcoholic extracts in a platinum

¹ Baly and collaborators: loc. cit.

dish. Molisch test for carbohydrate in the residue as such and Benedict's test after hydrolyzing the residue with hydrochloric acid gave negative results. The exact weights of the residue obtained in the main and control experiments are shown in the following table. There is practically no difference between the amounts of residue in the photosynthesis experiments and the blank ones.

TABLE IV

Experiment	Total residue in grms.	Residue from Methyl Alcohol	Net residue in grms.
1. 10 grms of NiCO_3 in 250 cc of conductivity water, agitated in the dark for two hrs.	0.0070	0.0006	0.0064
2. 10 grms of NiCO_3 in 250 cc of water — CO_2 passed for 2 hours in the dark	0.0084	0.0006	0.0078
3. 10 grms of NiCO_3 in 250 cc of water, simply exposed for 2 hrs.	0.0076	0.0006	0.0070
4. 10 grms of NiCO_3 in 250 cc of water — CO_2 passed in the exposed solution for 2 hrs.	0.0086	0.0006	0.0080

Further experiments with electrolytically prepared nickel carbonate and supported catalysts, described by Baly and his collaborators in their recent publication are being carried out, and will be reported in due course.

(d) *Chlorophyll.*

Reference to the work of those investigators who have used chlorophyll as a 'sensitizer' in their experiments on photosynthesis shows that in many cases little or no mention is made of the state of purity of the preparations used. By the word 'chlorophyll' one can mean anything from a mixture of all the plant pigments to a definite chemical compound known as chlorophyll a or b. In the experiments mentioned above, specially pure chlorophyll (a) was always employed. It was prepared from the dried leaves of a kind of Indian nettle which grows wild in this part of the country by following in every detail the method employed by Willstätter and Stoll in their well-known work and described by them in "Untersuchungen über die Assimilation der Kohlensäure," Berlin, 1918. 100 grms of the dried materials yielded 0.273 grams of the pure pigment. The extinction coefficients of its solution in pure acetone for lights of different wave-lengths were determined by a spectrophotometer of König and Martens type, made by Schmidt and Häensch (Berlin), using a pointolite lamp as a source of light. The results of these photometric measurements, given below, indicate two regions of highest absorption in the blue-violet and the red portion of the spectrum, at wave-lengths 432 and 641 $\text{m}\mu$, respectively. In addition to the above, there are four adsorption maxima at 497, 537, 578 and 613 $\text{m}\mu$. The region of least absorption lies in the yellow and green at 569 — 552 and 512 — 507 $\text{m}\mu$. These results are also shown graphically in the form of an absorption-curve, Fig. 1.

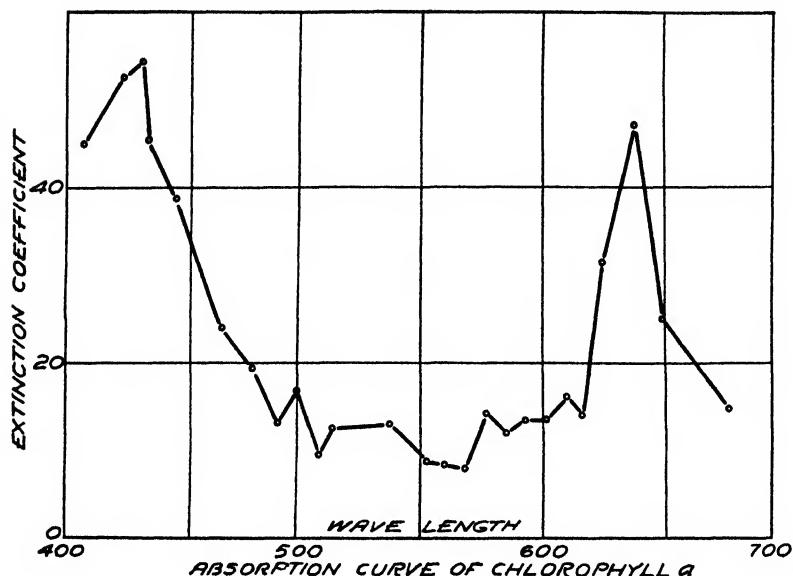


FIG. 1

TABLE V

Concentration—0.00486 per cent.

Thicknesses—2.5, 5.5, 12.5 cms.

No.	Wave-length	Extinction coefficient	No.	Wave-length	Extinction coefficient
1.	682.4 mμ	14.8	14.	537.2 mμ	12.95
2.	653.6 "	25.3	15.	512.2 "	12.44
3.	641.6 "	47.2	16.	507.2 "	9.38
4.	628.8 "	31.57	17.	497.2 "	16.86
5.	620.4 "	14.10	18.	489.0 "	13.25
6.	612.6 "	16.20	19.	478.8 "	19.40
7.	605.0 "	13.70	20.	465.8 "	23.50
8.	595.6 "	13.58	21.	447.6 "	38.87
9.	586.8 "	11.95	22.	434.4 "	47.10
10.	578.4 "	14.30	23.	432.8 "	54.20
11.	569.7 "	7.85	24.	423.6 "	52.85
12.	560.8 "	8.50	25.	407.2 "	45.10
13.	552.6 "	8.80			

In order to prepare a colloidal solution of chlorophyll *a*, the following procedure, recommended by Willstätter and Stoll, was adopted:—

100 cc of a solution of chlorophyll *a* in acetone were poured into a beaker of one litre capacity. 400 cc of conductivity water, after being boiled and suddenly cooled to 30° by immersion in a freezing mixture, were poured at once into the chlorophyll solution and the beaker was constantly shaken until the solution turned green. This solution was now distilled under reduced pressure

at $30^{\circ} - 35^{\circ}$, the receiver being placed in a mixture of salt and ice. As the distillation proceeded, more conductivity water was added from time to time by means of a thistle funnel, reaching to the bottom of the distilling flask. Within 3 to 4 hours, the whole of the acetone in the original solution was displaced by water. The distillation was continued until the distillate failed to give any test for acetone. The colloidal solution so prepared was coloured pure green and did not show any fluorescence.

Discussion

The results of our experiments on the action of heterogeneous and monochromatic ultra-violet light on carbonic acid in aqueous solution conclusively prove the incapacity of these radiations to bring about the required activation of carbonic acid. The positive tests for formaldehyde or sugars obtained by other investigators, were probably due either to the contamination of the materials used or to the lack of sufficient precautions in the application of the tests. Theoretical considerations too, rule out the possibility of obtaining positive results with the wave-length $313 \text{ m}\mu$. According to the thermochemical equation,



nearly 112,300 cals are required for the decomposition of one gram-molecule of carbonic acid.

This quantity of energy according to the quantum theory of photo-chemical action, must be present in N light quanta i.e.

$$112,300 \text{ cals} = N h \nu$$

putting the values of N (6.062×10^{23}) and the Planck constant h (6.547×10^{-27} ergs) the value of ν is found to be 1.18×10^{15} which corresponds to a wave-length of $255 \text{ m}\mu$. This means that radiations of wave-lengths greater than $255 \text{ m}\mu$ do not contain sufficient amount of energy to decompose carbonic acid molecule in one step into formaldehyde or sugar. We have tried the effect of radiations of wave-length $254 \text{ m}\mu$ without any positive result. The next experiments should be tried with radiations of $200 \text{ m}\mu$ which according to Baly¹ are capable of reducing carbonic acid to formaldehyde.

Attempts to achieve photosynthesis in the visible light fall into two groups. To the first group belong the experiments in which organic and inorganic substances have been employed as sensitizers or "photo-catalysts." The results of our experiments in this connection as detailed in Tables II and III stand in clear contradiction to those of G. Rao, A. Ram and Dhar.² Where formaldehyde has been detected in the exposed solutions containing CO_2 , it has been found in an almost equal amount in a blank experiment performed under identical conditions but without CO_2 . There is hardly any room left for doubt as to the source of small quantities of formaldehyde obtained in the experiments of the authors, quoted above. It is most probably derived either from impurities present in the preparations used or from the photo-decomposition

¹ Baly: J. Chem. Soc., 119, 1025 (1921).

² J. Phys. Chem., 35, 1418 (1931); 36, 567 (1932).

of the materials themselves. Merck's chemicals are generally despatched in glass containers having a coating of wax on the corks or stoppers. Special care has to be exercised in the opening of these containers, as even a small quantity of wax or cork material finding its way into the contents, can render them quite unsuitable for a work of this nature. As an instance of this error, reference may be made to the experiments of the present writers with solutions of sodium bicarbonate, mentioned in Table III. While positive tests were often obtained by the use of Merck's extra pure chemical, not a trace of formaldehyde was to be found when sodium bicarbonate prepared in the laboratory with all the necessary precautions, was employed. Further, especially purified nickel carbonate gave negative results, when illuminated in the presence of CO_2 , but the addition of a very small trace of grease led to a positive test for formaldehyde.

The danger of using organic substances such as chlorophyll, malachite green, methyl orange, and copper acetate, in experiments on photosynthesis in 'vitro,' is so obvious that one need not discuss it in any detail. Suffice it to say that all the four substances mentioned above, and a number of other organic compounds, give rise to formaldehyde under more or less strong illumination. A colloidal solution of chlorophyll a, prepared by the present writers by the method described above, gives positive indication of the formation of formaldehyde, both on illumination with CO_2 and without it. The same is the case with malachite green, methyl orange and copper acetate, the latter substance yielding comparatively large amounts of formaldehyde (see Table III).

In view of the above it is, therefore, not at all surprising that Atma Ram and Dhar should have obtained positive tests in their experiments referred to above, in which a current of CO_2 was passed in beakers containing chlorophyll, malachite green and copper acetate, suspended or dissolved in conductivity water and exposed to direct sunlight. No mention is made in the paper of Atma Ram and Dhar, of any blank experiment performed with the object of testing the action of light on these substances in the absence of CO_2 with the exception of a brief remark in the case of chlorophyll suspensions to the effect that formaldehyde was obtained in greater amount than when chlorophyll alone was exposed and distilled. The only reference to such control experiment is to be found in a previous paper by G. Rao and Dhar,¹ in which it is stated that comparative experiments were performed with chlorophyll and aniline dyes and in every case greater yields of formaldehyde were obtained in the presence of CO_2 , than without it. From this it is concluded that CO_2 is reduced to formaldehyde in the presence of these dyes. In view of the fact that it is extremely difficult if not impossible, to perform experiments in the sunlight under exactly identical conditions the above conclusion is hardly justified. The passage of CO_2 with the consequent stirring of the mixture produces a difference in the conditions of the two experiments, which can lead to erroneous results. The experiments performed by the present writers show

¹ G. Rao and Dhar: *J. Phys. Chem.*, **35**, 1418 (1931).

that the amounts of formaldehyde produced in the two cases, are the same within the experimental error.

The second group of experiments on 'photosynthesis in vitro' include those attempts in which coloured powders, capable of adsorbing carbonic acid on their surface, such as basic carbonates of nickel and cobalt have been employed. These experiments form a category by themselves because it is believed that in the presence of these surfaces, a molecule of carbonic acid is activated doubly; first through adsorption on the surface and secondly, through the absorption of the radiant energy. There are, no doubt, some good reasons in favor of this mode of approach to the problem and it receives a further support from the fact that photosynthesis in vivo is, to all appearance, a heterogeneous action taking place on the surface of the chloroplast in the leaves. But the present writers have so far failed to obtain any indication of photosynthesis by the use of these powders. It must, however, be admitted that the investigations of Baly and his collaborators open out vast possibilities of further research in this important line, which need be explored with increasing patience and skill. Further investigations on this line are being carried out in this laboratory, and will be reported in due course.

Summary

1. Experiments on the photochemical reduction of CO_2 in aqueous solution have been carried out in the ultraviolet, sunlight, and the light of tungsten filament lamps.

2. The results of experiments with heterogeneous and monochromatic ultra-violet light indicate that the light of wave-length $254 \text{ m}\mu$ is incapable of bringing about the required activation of carbonic acid.

3. Experiments, performed in direct sunlight with various inorganic and organic photosensitizers, suspended or dissolved in aqueous solutions of CO_2 , give no indication of the reduction of CO_2 under these conditions, thus contradicting the claims put forward by Dhar and collaborators.

4. The experiments of Baly and collaborators have been repeated, using specially purified and activated basic nickel carbonate, with negative results.

5. Chlorophyll (a) was prepared in a pure condition from the dried leaves of an Indian nettle, in accordance with the method of Willstätter and Stoll, and its extinction coefficients for light of different wave-lengths determined with the help of a spectro-photometer of König and Martens type.

The colloidal solution of chlorophyll (a), and the ordinary solutions of pure malachite green, methyl orange and copper acetate after exposure to sunlight in sealed bulbs from which CO_2 was excluded, were found to contain formaldehyde.

7. The results have been compared with those of other workers and possible causes of the discrepancies pointed out.

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STUDIES ON THE MECHANISM OF IONIC EXCHANGE IN COLLOIDAL ALUMINUM SILICATES*

BY HANS JENNY

Introduction

In 1819 the Italian chemist Gazzari⁴⁶ made the interesting observation that clay decolorizes liquid manure and retains soluble substances which in turn can be released to growing plants. Gazzari's work is perhaps the first study on exchange adsorption or ionic exchange which at present holds such a prominent place in general colloid chemistry. However, it was really the classical work of Thomas Way⁵² on "The power of soils to absorb manure" which, in 1850, stirred the agricultural chemists and divided them into two hostile camps in regard to the nature of these processes. So revolutionary were Way's discoveries from the viewpoint of soil fertility that he himself came to the conclusion: "It cannot be regarded in any other light than as a direct impress of the wonderful hand of providence."

Way was the originator of the following instructive experiment: If a solution of KCl percolates through a column of soil, differential adsorption takes place. Only the positive part of the salt (K) is retained, while the negative (Cl) remains in the soil solution. In the place of the adsorbed potassium another element, mostly Ca, appears in the liquid phase.

This replacement is "wonderful" indeed, since the valuable element K, indispensable for plant growth, is retained by the soil and prevented from leaching at the cost of the common element Ca. For 80 years this experiment has remained the corner stone of all investigations on base exchange in soils. It has been confirmed again and again in various modifications. There is no general agreement, however, as to the mechanism of the phenomenon. Way was inclined to believe that the process was a chemical one, although he was aware of certain abnormal, non-chemical characteristics such as speed of reaction, influence of temperature, existence of lyotropic series and others. Liebig,³¹ not knowing the law of mass action, vehemently opposed Way and advanced a physical explanation of adsorption. Since that time the disputation about the chemical or physical nature of base exchange in soils has not come to rest. The situation is quite similar to the one existing in the chemistry of proteins and in the explanation of adsorption in general colloid chemistry.

In studying the voluminous literature on ionic exchange one gains the impression that apparently the diversity of opinion is partly due to psychological prestige reasons, since the experimental material presented is in most cases not adequate to substantiate the conclusions drawn. Most of the workers picked up a random sample of soil and conducted experiments without

* Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Columbia, Mo. Journal Series No. 334.

knowing exactly what they were working with. Natural soils are too complicated and represent systems too variable to yield precise information about the mechanism of ionic exchange. Fortunately there are two promising ways to avoid this uncertainty of the nature of the adsorbent. One is the study of ionic exchange with artificial clays (zeolites, permutits); the other is the isolation of the colloidal fraction from soil and its subsequent purification by methods which do not affect the nature of the colloid. A systematic study with such artificial and purified colloids in which both the nature of the colloidal complex and the properties of the participating ions are considered should reveal a qualitative and quantitative insight into the mechanism of ionic exchange. Such was the aim of the investigation herewith reported.

Practical Significance of Ionic Exchange.

Aside from theoretical interest, ionic exchange is of far-reaching importance in soil studies and in many industrial problems. The fixation of fertilizers added to the soil is still the classical problem of applied ionic exchange. The ions adsorbed in soils can be easily utilized by plants; in the process of the liberation of nutrients by living organisms ionic exchange undoubtedly plays a very significant rôle.

It is being realized more and more that there is a relation between ionic exchange and soil formation. The first step in the weathering of aluminum silicates is an ionic exchange in which the hydrogen ions of water and carbonic acid replace the cations on the surface of the crystal lattice of the minerals. The differential leaching of K, Na, Ca, Mg, from soils is easily understood on the basis of the behavior of cations in the exchange adsorption.²⁵ Gedroiz²⁰ has even gone so far as to propose a scheme of soil classification which is based on the nature of the adsorbed ions on the colloidal soil complex. The great problem of the reclamation of alkali soils is now more fully understood. The important investigations of Gedroiz,²⁰ Sigmond,⁴⁷ Kelley,²⁷ Burgess¹² and others have shown that ultimately it is a base exchange reaction on a very huge scale.

Physical, as well as chemical, properties of soils are closely associated with exchange adsorption. Wiegner⁵⁹ and his pupils have been able to show that coagulation, dispersion, viscosity, hydration and structure of colloidal clays are greatly affected by the nature of the adsorbed ions. These observations have been confirmed by Bayer¹ and others.

A direct consequence of base exchange studies with clays has been the invention of water softening³⁵ by the zeolite or permutit process, in which Ca-ions of the water are exchanged against Na-ions of the aluminum silicate. In sugar factories the principle of base exchange has become a vital factor in the development of refining methods. There are yet many possibilities for the application of base exchange in industry, such as in the tanning of leather, stabilization of emulsions and suspensions in general, manufacturing of milk products and others.

The Nature of the Colloidal Complex.

Colloidal clays found in natural soils exhibit crystalline properties. On the basis of Debye-Scherrer diagrams the presence of montmorillonite, beidellite, halloysite and bauxite in soils has been definitely established.^{22,28} Fortunately, the recent work of Bragg¹⁰ and Pauling⁴⁸ permits a deeper insight into the nature of these colloidal complexes. According to these investigators silicates are made up of ions which act as impenetrable spheres with characteristic diameters. On account of their abundance and large size the oxygen ions ($r = 1.32\text{\AA}$) play an important rôle in the structure of aluminum silicates. The small but highly charged $\text{Si}^{++++}(r = 0.39\text{\AA})$ and $\text{Al}^{+++}(r = 0.57\text{\AA})$ ions are surrounded by four or six oxygen ions forming tetrahedrons or octahedrons which are considered the "building stones" of aluminum silicates. The remaining electric valence forces of the O^{--} ions are saturated by cations (K^+ , Ca^{++}) which are packed in the interstices of the oxygen polyhedrons. The crystal is held together by the electrostatic forces existing between cations and anions. The packing of the building stones can be close or open. St. Naray-Szabo³⁷ expresses the density of the packing quantitatively by the "volume" occupied by one oxygen ion. From the viewpoint of ionic exchange it is very significant to note that mainly such crystallized aluminum silicates as have an open packing are distinctly capable of base exchange and adsorption. In the following selected list (Table I) the correlation between density of packing and ionic exchange capacity is indicated:

TABLE I
Packing of Oxygen Ions and Intensity of Ionic Exchange

Mineral	Formula	Volume per oxygen ion \AA^3	Ionic exchange
Corundum	Al_2O_3	14.0	Very little or none
Quartz	SiO_2	18.7	Little
Muscovite	$\text{K}(\text{Al}_2\text{Mg}_3)(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	19.2	Distinct
Nosean	$\text{Na}_6\text{Al}_6(\text{SiO}_4)_{6.2}\text{Na}_2\text{SO}_4$	23.1	Pronounced
Ultramarine	" " " "	23.1	Very pronounced

Pronounced ionic exchange is observed mainly in the natural and artificial zeolites which have such big interstices that large ions such as K^+ and Ba^{++} , as well as H_2O molecules can move freely in the interior of the crystals. Crystals with close packing exchange only at their outer surfaces. Their ability to adsorb ions depends, therefore, on the size of the colloidal particles. Thus, Kelley²⁸ was able to increase the exchange capacity of bentonite clays by mere grinding in a ball mill. On the other hand, Wiegner⁵⁵ demonstrated that in case of permutit gels (related to ultramarine in the above table) the degree of dispersion is without material effect upon ionic exchange. The importance of crystal structure in relation to ionic exchange is illustrated convincingly in Figs. 1 to 3. Al_2O_3 and SiO_2 simply do not permit ions to enter the crystals on account of the architectural arrangement of the oxygen ions. In the case of ultramarine the pattern of alternating aluminum and silicon tetrahedra

furnishes large cavities consisting of a cubical space with an edge of 3.7\AA and six crosswise arranged prolongations in which there is superfluous space for "wandering" constituents.²⁸

On the basis of these modern pictures of aluminum silicates ionic exchange can be much better visualized than has been hitherto possible. The electro-negatively charged framework of O^{--} and possibly OH^- ions acts as the attractive wall (inner layer of the Helmholtz double

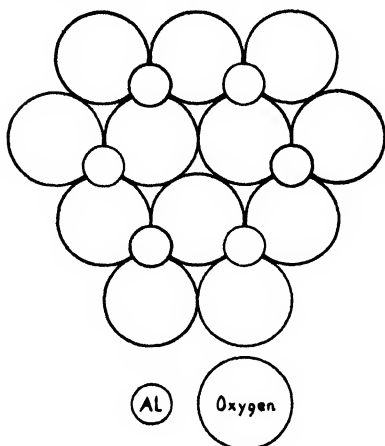


FIG. 1

Structure of aluminum oxide (Al_2O_3).
Close packed system (Bragg¹⁰).

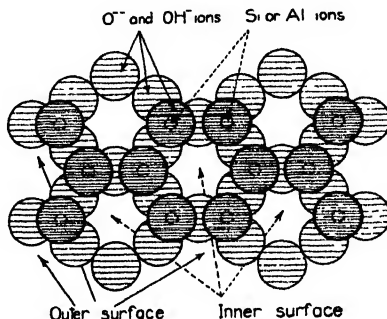


FIG. 2

Arrangement of oxygen ions in an open packed system (St. Naray-Szabo²⁷).

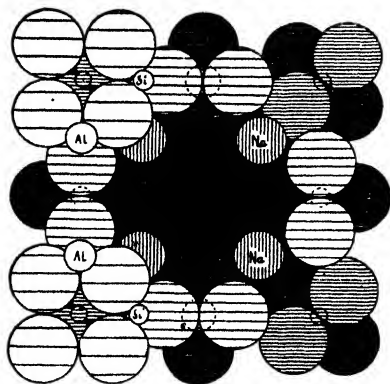


FIG. 3

Structure of ultramarine (Jaeger²³).
The large circles represent oxygen ions.
Note the big cavity in the interior of the cell containing exchangeable Na ions.

layer) for the adsorption of cations. The structural arrangement of the O^{--} ions remains undisturbed as long as the positive and negative electrical charges are balanced. The forces of attraction are mainly electrostatic in nature (except perhaps of H^+) and are greater the closer the cations can approach the oxygen ions. It is to be expected, therefore, that ions of different size and electric charge act differently both in their adsorption and release. The search for such relationships between ionic exchange and properties of the ions was one of the main objects of this investigation.

Presentation of Experimental Material*

In these investigations ionic exchange studies were made on both artificial and natural colloidal aluminum silicates. *Artificial aluminum silicates:* Ordinary permutits furnished by J. D. Riedel in Berlin and Folin-permutit obtained from Arthur H. Thomas Company were converted into pure

* Credit for part of the experimental work is due to E. R. Shade and W. H. Allison.

TABLE II

System: NH_4 - permutit (Riedel) + monovalent cations. 1 g. permutit containing 4.15 millequivalents exchangeable NH_4 ; volume 100 cc.; time of reaction 8-10 days; room temperature. $y\%$ = NH_4 exchanged in percentage of total exchangeable NH_4 . a = millequivalents of salt added.

NH ₄ -permutit (Riedel) + LiCl	NH ₄ -permutit (Riedel) + NaCl		NH ₄ -permutit (Riedel) + KCl		NH ₄ -permutit (Riedel) + RbCl		NH ₄ -permutit (Riedel) + CsCl		NH ₄ -permutit (Riedel) + HCl		
	y%	a	y%	a	y%	a	y%	a	y%	a	
19.75	5.42	28.11	2.00	33.98	2.01	38.95	1.95	30.96	2.01	47.95	2.93
29.64	13.55	34.70	5.00	52.53	5.03	58.31	4.90	62.65	5.02	82.65	7.33
33.01	27.10	45.06	10.00	66.26	10.06	71.08	9.79	73.73	10.05	92.30	14.65
42.65	67.75	66.50	50.00	79.04	25.15	86.75	24.48	93.97	25.31	100.00	36.62
52.77	135.50	76.39	100.00	87.47	50.30	—	—	—	—	—	—
—	—	—	—	90.84	100.60	—	—	—	—	—	—

TABLE III

System: NH_4 - permutit (Folin)¹ + monovalent cations. 0.629 g. NH_4 - permutit containing 2.07 millequivalents exchangeable NH_4 ; volume 250 cc.; time of reaction one week; room temperature. $y\%$ = NH_4 exchanged in percentage of total exchangeable NH_4 . a = millequivalents of salt added.

NH ₄ -permutit (Folin) + LiCl			NH ₄ -permutit (Folin) + NaCl			NH ₄ -permutit (Folin) + KCl			NH ₄ -permutit (Folin) + HCl		
y%	a	pH of su- pernatant liquid	y%	a	pH of su- pernatant liquid	y%	a	pH of su- pernatant liquid	y%	a	pH of su- pernatant liquid
8.53	1.171	7.13	24.04	1.000	6.91	31.56	1.004	7.50	40.60	0.963	6.55
19.28	2.928	7.15	38.55	2.500	—	50.38	2.509	6.95	83.90	2.407	—
25.08	5.856	7.15	53.04	5.000	7.15	69.66	5.018	6.82	97.10	4.814	3.61
35.18	14.640	7.08	60.60	12.499	6.89	83.96	12.545	7.26	98.75	12.035	2.37

¹This NH_4 -permutit contains small amounts of exchangeable H-ions.

TABLE IV

System: $NH_4 - H - Putnam\ clay + monovalent\ cations$. 6.909 g. colloid containing 2.070 milliequivalents exchangeable NH_4 ; volume 500 cc., time of reaction 10 days, room temperature. $y\% = NH_4$ exchanged in percentage of total exchangeable NH_4 . a = milliequivalents of salt added.

$NH_4 - H - Putnam\ clay + LiCl$			$NH_4 - H - Putnam\ clay + NaCl$			$NH_4 - H - Putnam\ clay + KCl$			$NH_4 - H - Putnam\ clay + HCl$		
$y\%$	a	pH of super- of sol liquid	$y\%$	a	pH of super- of sol liquid	$y\%$	a	pH of super- of sol liquid	$y\%$	a	pH of super- of sol liquid
34.40	1.171	5.20	27.62	1.078	5.24	37.72	1.004	5.16	52.18	0.963	4.70
40.72	2.928	5.20	39.45	2.695	5.24	57.95	2.509	4.90	87.32	2.407	3.53
50.38	5.856	4.95	50.50	5.389	4.81	70.23	5.018	4.62	90.30	4.814	2.76
63.81	14.640	4.62	62.85	13.473	4.78	78.92	12.545	4.24	93.92	12.035	2.13
72.80	29.280	4.44	73.28	26.945	4.49	91.28	25.090	4.10	95.50	24.070	1.69

TABLE V

System: $NH_4 - Putnam\ clay + monovalent\ cations$. 4.955 g. colloid containing 4.115 milliequivalents NH_4 ; volume 500 cc., time of reaction 7 days, room temperature; pH of sol = 8.56. $y\% = NH_4$ exchanged in percentage of total exchangeable NH_4 . a = milliequivalents of salt added.

$NH_4 - Putnam\ clay + LiCl$			$NH_4 - Putnam\ clay + NaCl$			$NH_4 - Putnam\ clay + KCl$		
$y\%$	a	pH of super- of sol liquid	$y\%$	a	pH of super- of sol liquid	$y\%$	a	pH of super- of sol liquid
37.78	2.654	7.7	33.73	2.000	7.3	50.94	1.945	8.3
44.07	6.636	7.1	43.74	5.000	7.0	74.12	4.862	7.9
50.85	13.272	7.1	49.14	10.000	8.0	85.77	9.723	8.1
64.94	33.180	6.9	61.65	24.997	8.0	96.77	24.308	7.9
69.26	66.360	6.7	67.06	49.995	7.0	99.20	48.615	7.7

TABLE VI

System: $NH_4 - H - \text{Putnam Soil} + \text{monovalent cations}$. 10 g. of soil containing 2.279 milliequivalents exchangeable NH_4 ; volume 250 cc., time of reaction one week, room temperature. $y\% = NH_4$ exchanged in percentage of total exchangeable NH_4 . $a =$ milliequivalents of salt added.

$NH_4 - H - \text{Putnam soil} + LiCl$			$NH_4 - H - \text{Putnam soil} + NaCl$			$NH_4 - H - \text{Putnam soil} + KCl$			$NH_4 - H - \text{Putnam soil} + HCl$		
$y\%$	a	pH of sol	$y\%$	a	pH of sol	$y\%$	a	pH of sol	$y\%$	a	pH of sol
25.81	1.171	5.60	25.81	1.000	5.44	34.41	0.972	5.34	37.26	0.963	4.15
37.26	2.928	5.24	37.26	2.450	5.20	37.35	2.431	4.84	65.95	2.407	3.02
45.86	5.856	5.10	43.01	5.000	5.00	68.82	4.862	4.78	82.86	4.814	2.22
54.48	14.640	4.74	48.74	12.499	4.70	77.42	12.154	4.55	91.75	12.035	—

TABLE VII

System: $NH_4 - H - \text{bentonite} + \text{monovalent cations}$. 2.850 g. colloid containing 2.195 milliequivalents exchangeable NH_4 ; volume 500 cc., time of reaction one week; temperature 28°C. $y\% = NH_4$ exchanged in percentage of total exchangeable NH_4 . $a =$ milliequivalents of salt added.

$NH_4 - H - \text{bentonite} + LiCl$			$NH_4 - H - \text{bentonite} + NaCl$			$NH_4 - H - \text{bentonite} + KCl$			$NH_4 - H - \text{bentonite} + HCl$		
$y\%$	a	pH of sol	$y\%$	a	pH of sol	$y\%$	a	pH of sol	$y\%$	a	pH of sol
56.47	1.171	6.02	45.15	1.000	5.32	48.36	0.988	6.10	47.72	0.963	4.55
65.62	2.928	6.30	53.85	2.500	6.18	54.02	2.270	5.75	69.25	2.407	2.80
76.08	5.856	5.92	59.68	5.000	5.93	67.55	4.940	5.95	87.20	4.814	2.29
85.55	14.640	5.42	76.70	12.499	5.60	91.25	12.349	5.44	99.70	12.035	1.80
96.18	29.280	5.55	87.75	24.998	5.08	101.20	24.699	5.05	101.40	24.070	1.50

Li-Na-K-NH₄-permutits by leaching with chlorides for several months as previously described.²⁴ H-permutit was prepared by electrodialysis in a Bradfield three compartment cell.⁶

Natural aluminum silicates. Adopting the method of Bradfield,⁴ soil collected from the B-horizon of the Putnam silt loam was churned and after standing for several days was run through a supercentrifuge in order to isolate the colloidal particles. According to the data of Bayer¹ these are of the dimensions of 100-150 mμ (φ). Electrodialysis in Bradfield cells converted the clays, which originally contained various exchangeable cations, into pure hydrogen systems. Pure basic clays were then obtained by adding the proper amounts of LiOH, NaOH, KOH, or NH₄OH to the H-clays. Corresponding samples of bentonite clays from Wyoming were prepared in the same way. The amount of base added was equal to the saturation capacity of the clays which was determined by titration curves according to Bradfield⁷ and by replacement of H⁺ by KCl. Both methods gave very similar results.

The *exchange experiments* were conducted as follows: stock solutions of clay sols (3-5%) were transferred into volumetric flasks (250, 500 cc.), and redistilled, carbon dioxide-free water was added nearly up to the graduation mark. These colloid-water systems were kept for a week in a constant temperature room in order to permit the colloidal particles to reach the hydration

TABLE VIII

System: *NH₄-bentonite + monovalent cations.* 1.770 g. colloid containing 1.980 milliequivalents NH₄; volume 500 cc., time of reaction 10 days, room temperature; pH of sol = 8.56, y% = NH₄ exchanged in percentage of total NH₄. a = milliequivalents salt added.

NH ₄ -bentonite + LiCl			NH ₄ -bentonite + NaCl			NH ₄ -bentonite + KCl		
y%	a	pH of sol	y%	a	pH of sol	y%	a	pH of sol
69.75	3.56	—	70.25	5.04	8.15	78.34	5.02	8.14
81.37	8.89	—	80.86	12.59	8.05	84.90	12.55	8.20

TABLE IX

System: *H-permutit + monovalent cations.* 2.500 g. permutit containing 1.743 milliequivalents exchangeable H⁺; volume 125 cc., time of reaction one week, temperature 26°C. y% = H⁺ exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H-permutit + LiCl			H-permutit + NaCl			H-permutit + KCl		
y%	a	pH of super- natant liquid	y%	a	pH of super- natant liquid	y%	a	pH of super- natant liquid
1.13	2.135	5.00	2.69	2.014	4.75	7.92	2.008	—
1.41	5.338	4.91	3.20	5.035	4.70	11.01	5.020	—
2.54	10.677	4.88	4.52	10.070	4.64	15.55	10.040	—
3.11	21.354	4.86	6.51	20.140	4.52	20.88	20.080	—

TABLE X

System: *H-Putnam clay + monovalent cations*. 3.330 g. *H*-colloid containing 1.881 milliequivalents exchangeable H^+ ; volume 250 cc.; time of reaction one week, temperature 28°C. $y\%$ = H^+ exchanged in percentage of total exchangeable *H*. *a* = milliequivalents of salt added.

<i>H</i> - Putnam clay + LiCl				<i>H</i> - Putnam clay + NaCl				<i>H</i> - Putnam Clay + KCl			
$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid	$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid	$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid
7.34	2 135	3.90	4.00	6.54	2.014	3.92	3.92	15.71	2.008	3.72	3.67
11.01	5.338	3.80	3.92	11.01	5.035	3.80	3.81	27.22	5.020	3.59	3.64
15.74	10.677	3.74	3.82	15.73	10.070	3.73	3.75	41.35	10.040	3.57	3.62
25.36	21.354	3.70	3.74	26.70	20.140	3.69	3.70	59.70	20.080	3.54	3.59
32.75	32.031	3.69	3.72	35.08	30.210	3.65	3.66	73.30	30.120	3.57	3.56

TABLE XI

System: *H-bentonite + monovalent cations*. 2.210 g. *H*-colloid containing 1.872 milliequivalents exchangeable *H*; volume 250 cc.; time of reaction one week; temperature 28°C. $y\%$ = *H* exchanged in percentage of total exchangeable *H*. *a* = milliequivalents of salt added.

<i>H</i> - bentonite + LiCl				<i>H</i> - bentonite + NaCl				<i>H</i> - bentonite + KCl			
$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid	$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid	$y\%$	<i>a</i>	pH of sol	pH of super-natant liquid
12.32	0.712	3.20	3.18	15.81	2.014	3.05	2.67	15.16	0.972	3.13	3.34
17.58	1.778	3.02	3.04	17.58	2.500	2.98	3.10	19.47	2.008	2.85	2.90
18.43	2.135	2.90	3.10	20.78	5.035	2.80	3.00	24.60	4.860	—	2.84
23.13	5.338	2.85	2.97	26.28	10.070	2.77	2.93	32.63	10.040	2.72	2.84
27.09	10.677	2.76	2.94	29.68	12.500	—	—	35.20	12.150	2.75	2.71
32.10	17.780	2.70	2.86	34.20	20.140	2.65	3.02	45.60	24.300	2.71	2.60
32.60	21.354	2.76	2.98	37.60	25.000	—	—	46.89	20.080	2.74	2.85
39.75	32.031	2.87	3.18	43.65	30.210	2.72	—	62.60	30.120	2.76	2.90

TABLE XII

System: *H-Sharkey clay + monovalent cations*. 2.366 g. H-colloid containing 1.908 milliequivalents exchangeable H; volume 250 cc.; time of reaction 10 days; room temperature. $y\%$ = H exchanged in percentage of total exchangeable H. a = milliequivalents of salt added.

H - Sharkey clay + LiCl			H - Sharkey clay + NaCl			H - Sharkey clay + KCl		
$y\%$	a	pH of sol	pH of super-natant liquid	$y\%$	a	pH of sol	pH of super-natant liquid	pH of sol
11.32	2.848	—	3.55	10.80	2.014	3.63	3.56	15.52
14.98	5.694	—	3.50	15.52	5.036	3.50	3.50	23.28
18.03	9.966	—	3.53	18.56	10.070	3.63	3.50	34.58
25.78	21.354	—	3.42	27.26	20.140	3.37	3.49	50.62
								20.072
								3.29
								3.49

TABLE XIII

System: *Li, Na, K-Putnam clay + HCl (old sols)*. 1.420 g colloid containing 0.8075 milliequivalents exchangeable bases, volume 250 cc., time of reaction one week, temperature 28°C. $y\%$ = base exchanged in per cent, as determined by HCl adsorption. a = milliequivalents of HCl added.

Li - Putnam clay + HCl		Na - Putnam clay + HCl		K - Putnam clay + HCl	
$y\%$	a	$y\%$	a	$y\%$	a
45.88	0.3774	45.73	0.3774	42.80	0.3774
78.70	0.8075	80.30	0.8075	69.55	0.8075
84.82	1.496	86.03	1.496	80.43	1.496

TABLE XIV

System: Li, Na, K, H-Putnam clay + NH₄Cl (young, 4 day old sols). 7.5 g. Putnam clay containing 4.50 milliequivalents exchangeable cations; volume 500 cc.; time of reaction one week; temperature 25-28°C. y% = percentage of adsorbed ions released as determined by NH₄ - determination of the supernatant liquid before and after exchange reaction. a = milliequivalents NH₄Cl added.

Li - Putnam clay - NH ₄ Cl				Na - Putnam clay - NH ₄ Cl				K - Putnam clay + NH ₄ Cl				H - Putnam clay + NH ₄ Cl			
y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid
41.12	2.25	6.75	6.90	40.23	2.25	6.96	7.00	30.22	2.25	6.82	7.20	5.34	2.25	3.65	3.67
57.08	4.50	6.75	7.01	58.90	4.50	6.80	6.90	42.03	4.50	6.75	6.90	9.12	4.50	3.63	3.60
66.28	9.00	6.46	6.92	68.02	9.00	6.52	6.40	52.45	9.00	6.55	6.70	11.33	9.00	3.58	3.56
68.22	18.00	6.22	6.75	65.60	18.00	6.22	6.33	59.40	18.00	6.31	6.26	8.45	18.00	3.54	3.61
62.24	36.00	6.10	6.25	62.25	36.00	6.10	6.10	36.92	36.00	6.02	6.09	21.93	36.00	3.54	3.51

TABLE XV

System: Li, Na, K, H-bentonites + NH₄Cl (young, 4 day old sols). 5 g. bentonite clay containing 4.50 milliequivalents exchangeable cations; volume 500 cc.; time of reaction one week; temperature 25-28°C. y% = percentage of adsorbed ions released as determined by NH₄ - determination of the supernatant liquid before and after exchange reaction. a = milliequivalents NH₄Cl added.

Li - bentonite + NH ₄ Cl				Na - bentonite + NH ₄ Cl				K - bentonite + NH ₄ Cl				H - bentonite + NH ₄ Cl			
y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid	y%	a	pH of sol	pH of super-natant liquid
37.12	2.25	6.64	7.32	31.91	2.25	6.60	6.80	26.65	2.25	6.50	7.03	11.05	2.25	2.94	3.08
46.52	4.50	6.50	7.03	49.95	4.50	6.32	6.86	43.75	4.50	6.35	7.01	14.45	4.50	2.86	3.00
68.42	9.00	6.31	7.15	70.87	9.00	6.12	6.72	61.73	9.00	6.16	6.89	20.48	9.00	2.80	2.94
78.85	18.00	5.91	6.66	78.67	18.00	5.92	6.60	69.84	18.00	6.16	6.83	38.13	18.00	2.78	2.89

equilibrium. This precaution is necessary since it had been found that by diluting concentrated clay sols the hydration of the colloidal particles may become so strong as to bring about apparent negative adsorption. After equilibrium had been reached, neutral salt solutions (0.1-1.0 normal) were added and the flasks filled with water up to the graduation mark. After a week's standing at constant temperature (within $\pm 1^\circ\text{C}$) during which time the flasks were shaken daily, the colloidal particles were separated from the liquid by centrifuging or ultrafiltration.

The amount of ions exchanged was either found by direct determination (in release of ions) or by difference (in adsorption of ions). NH_4 was determined by distillation (occasionally also Nessleration); K was analyzed by the chloroplatinic method; and H was determined by titration using cresolphthalein as an indicator. Since the supernatant liquid of the H-systems treated with chlorides always contained Al^{+++} , titration of H^+ had to be made in the presence of AlCl_3 . Extensive titration with mixtures of HCl , AlCl_3 and LiCl , NaCl , KCl showed that the endpoint is reached at pH 9.2 which is in good agreement with the data reported by Britton.¹¹ All experiments reported were entirely repeated at least twice.

TABLE XVI

System: Li, Na, K-bentonite + HCl (old sols)

0.950 g. colloid containing 0.8075 milliequivalents exchangeable bases, volume 250 cc., time of reaction one week, temperature 28°C . y% = bases exchanged in per cent, as determined by HCl adsorption.

a = milliequivalents of HCl added.

Li-bentonite + HCl		Na-bentonite + HCl		K-bentonite + HCl	
y%	a	y%	a	y%	a
43.85	0.404	42.65	0.404	39.96	0.404
59.83	0.808	60.40	0.808	50.36	0.808
70.58	1.615	69.10	1.615	59.41	1.615

TABLE XVII

Release of adsorbed Li, Na, and K, ions against HCl (Young sols)

Fifty cc. of electrodialyzed H-bentonite (1.11 g. colloid) and 30.82 cc. of H-Putnam clay (1.65 g. colloid) were each diluted with 180 cc. H_2O . After 24 hours 0.936 milliequivalents of LiOH , NaOH , KOH , respectively, were added and the resulting *salt clays* were shaken daily for a week; 0.936 milliequivalents of HCl were then added and all systems were brought to a volume of 250 cc. After 9 days the sols were centrifuged and the HCl remaining in the clear supernatant liquid was determined by titration. The following results were obtained:

Li-bentonite + HCl = 77.90%	exchanged (symmetry value)		
Na-bentonite + HCl = 76.41%	"	"	"
K-bentonite + HCl = 74.12%	"	"	"
Li-Putnam clay + HCl = 84.48%	"	"	"
Na-Putnam clay + HCl = 86.10%	"	"	"
K-Putnam clay + HCl = 80.90%	"	"	"

TABLE XVIII

Release of adsorbed Li, Na, K from permutits by HCl
 1 g. permutit in 100 cc. volume; time of reaction
 one week; room temperature

Nature of permutit	Milliequivalents of exchangeable bases in 1 g. permutit	Milliequivalents HCl added	Percent exchanged (Symmetry value)
Li-permutit I	1.78	1.78	82.05%
Na-permutit I	2.34	2.34	77.40%
K-permutit I	1.64	1.64	73.20%
Na-permutit II	2.72	2.72	89.98%
K-permutit II	2.72	2.72	85.45%

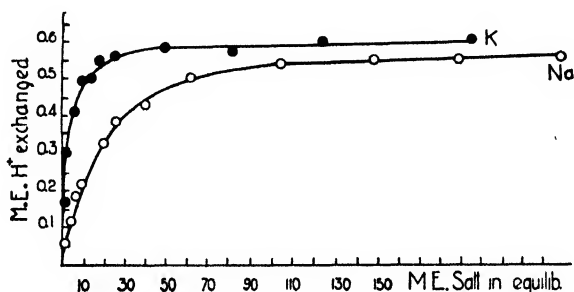


FIG. 4

Adsorption of cations by H-Putnam clay. (1 gr clay plus increasing amounts of NaCl, KCl.)

Mathematical Formulation of the Process of Ionic Exchange

The magnitude of ionic exchange is among other things a function of the amount of the salt added. Most investigators have been working with moderate concentrations only, omitting very dilute or highly concentrated systems. The neglect of including wide concentration ranges has been in many instances the direct cause of fruitless disputations as to the chemical or physical nature of the exchange process. There is no question that in all systems studied ionic exchange reaches a distinct maximum at which further additions of neutral salts remain ineffective in releasing adsorbed ions (See Fig. 4). The maximum (flat branch of the curve), however, does not necessarily correspond to the total exchange capacity of the colloid. Removal of released ions and repeated additions of electrolyte will in many cases liberate additional amounts of adsorbed ions until the absolute exchange maximum is reached.

For permutits the maximum exchange capacity lies between 400-500 milliequivalents of cations per 100 g. colloid, depending upon the preparation of the material. In many cases the cation-aluminum ratio in permutits is one. Natural clays contain considerable inert material and have much lower exchange capacities. The values found by the author are 85-100 milliequivalents of base for bentonites and 55-70 for Putnam clays as determined by

continuous leaching with neutral salts, or potentiometric titration of H-systems with $\text{Ca}(\text{OH})_2$ up to pH 7.

It is always necessary to state the methods used in determining the total ionic exchange capacity of a colloid, since not all methods give concordant results. There is considerable controversy among soil scientists as to the "correct" method of measuring the exchange capacity.

A considerable number of equations have been used to describe the functional relationships in ionic exchange reactions. Some of these are entirely empirical; others are supported by more or less convincing theoretical reasoning (Ganssen, Wolf, Freundlich, Rothmund and Kornfeld, Schmidt, Arrhenius, Wiegner, Vageler). The following three widely used formulae will be considered: *Ganssen's* equation*.¹⁹ On the basis of the law of mass action Ganssen derived the following formula:

$$K = \frac{x^2}{(m \cdot n - x)(g - x)}$$

where K = equilibrium constant,

m = exchange complex (permutit) in g,

n = total amount of exchangeable bases in the exchange complex,

g = total amount of salt in solution,

x = amount adsorbed.

Wiegner's equations.^{55,57} Wiegner, who approached base exchange from the colloid-chemical viewpoint, found that Freundlich's parabolic isotherm was able to describe satisfactorily the exchange reactions:

$$x/m = k \cdot c^{1/p}$$

where x/m = adsorbed amount per g. of adsorbing substance,

c = concentration of added salt after equilibrium has been reached,

k, p = constants.

Later Wiegner²⁴ modified the equation in order to express the fact that ionic exchange is independent of dilution:

$$\frac{x}{m} = k \left(\frac{c}{a - c} \right)^{1/p}$$

where a = concentration of salt added at the beginning of the reaction.

Vageler's equation.⁵⁰ Recently Vageler has suggested a new equation which expresses the observation that under higher concentrations the ionic exchange reaches a maximum:

$$y = \frac{x \cdot S}{x + C}$$

y = amount adsorbed per g. adsorbing substance,

x = amount of salt in equivalents added per g. adsorbent,

S = maximum exchange capacity (saturation capacity),

C = half value, that is the conc. of x at which 50% of S is exchanged.

* H. W. Kerr's²⁹ "new" theory and equation of base exchange are identical with the work of Ganssen, published twenty years ago.

This hyperbolic equation is identical in form with the well-known adsorption isotherm of Langmuir. The latter corresponds in a way to the law of mass action of surface reactions (Pauli).⁴⁰

In the present study all three types of equations have been used to describe the experimental data, but no equation has proved entirely satisfactory. It depends on how wide a range in concentration is investigated and what ions are included. In dilute to moderate concentrations of ions with low atomic weights the Freundlich-Wiegner equation is very valuable, but at higher concentrations, especially for larger ions, (including H) the formula fails. Here the Vageler-Langmuir equation proves to be more satisfactory. No equation is able to characterize, for instance, the finer differences existing between closely related ions, such as Na and Li in the case of exchange with H-clay. An equation which embraces the behavior of several cations at various concentrations would have to contain more parameters than just one or two. This, of course, would render the physical interpretation of the constants difficult.

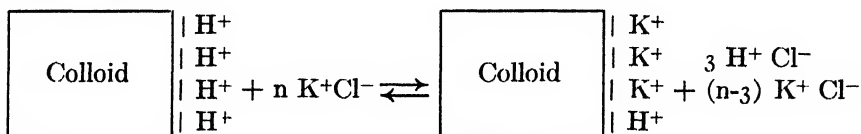
In order to numerically characterize the individual behavior of various ions a single magnitude would be extremely desirable. For this purpose a single point on the exchange curve must be used, since no satisfactory formula having but one parameter exists. The numerical magnitude selected in this study is called "*symmetry value*." It expresses the intensity of ionic exchange in percentage when the number of ions added to the system is made equal to the total number of exchangeable ions on the colloidal complex. For example, 100 grams of colloidal clay containing 60 milliequivalents of exchangeable NH_4 are mixed with a solution of NaCl having 60 milliequivalents of Na. Ionic exchange takes place and the Na ions replace 20 milliequivalents of NH_4 ions. The symmetry value is then $20/60 \cdot 100 = 33.33\%$. It is of interest to note that this symmetry value is in many cases approximately identical with the magnitude of the constant k in the Freundlich-Wiegner adsorption isotherm.

It might be worth while in this connection to point out a principal difficulty in the formulation of equations for base exchange reactions. Investigators who approach ionic exchange reactions on colloidal clays from the classical chemical standpoint often express the concentration of exchangeable cations as equivalents per total volume of the sol, as for instance, "one milliequivalent of hydrogen ions in 1000 cc. clay-suspension" (pH 3). In formulating equations for such "solutions" the exchangeable ions are treated as if they were uniformly distributed in the entire volume of the sol. But such is certainly not the case. The cations do not move at liberty in the solution. They are assembled on the surface of the suspended colloidal particles and are much closer together than the common concentration expression (pH 3 in the above case) indicates. In other words, the exchange reactions on the micelle occur in *concentrated* rather than in dilute ~~solutions~~ even if only one single colloidal particle were suspended in a liter of water. Attempts to measure the order of magnitude of ion concentrations on permutit surfaces lead to values $> 1-2$ normal. Under such circumstances the laws of classical chem-

istry which apply only to dilute solutions cannot be expected to yield good quantitative results. The "constants" in the equations may not be constants. The formulae will have to be modified. Inter-ionic effects and polarization phenomena must be taken into consideration and individual ionic properties such as charge, radius and electric field strength will certainly play an important rôle. It will be shown in the following discussion that a mere application of the laws of dilute solutions can embrace but a small part of the multitude of reactions encountered in ionic exchange.

The Avidity of the Colloidal Complex as a Factor in Ionic Exchange

If natural clays and artificial aluminum silicates are subjected to electro-dialysis they take up exchangeable hydrogen ions. The H-systems are usually called H-clay, H-permutit, etc. The pH of such systems depends upon the concentration of the solid phase present as shown by many investigators, notably by Bradfield.⁵ Wiegner⁵⁸ and Pallmann³⁸ have recently investigated in great detail this phenomenon and distinguish in such systems two types of hydrogen ions, "free ions," which are in true solution (very small in number), and "swarm ions," which are on the surface of the colloidal particles moving and sedimenting with them. From a theoretical standpoint it is of great interest to note that the adsorbed H-ions also affect the H₂-electrode as well as invert sucrose. Upon addition of a neutral salt ionic exchange occurs, the cation of the salt taking the place of the hydrogen ion on the colloid. The H-ions enter the intermicellar liquid and can be determined (by titration) after separation of the solid from the liquid phase by centrifuging or ultrafiltration. Using Zsigmondy's notation, the reaction can be written as follows:



The nature of the inner layer (negative sign) is not indicated in the above equation. It is assumed that it consists mainly of negatively charged O⁻⁻ and OH⁻ ions.

Colloidal clays show great differences in the amount of hydrogen ions released. This is well illustrated in Fig. 5, which shows the amount of H⁺ released from five grams of H-colloid upon addition of various amounts of KCl. The number of hydrogen ions freed depends, of course, upon the number of exchangeable H-ions adsorbed per unit colloid (capacity factor) and *also upon the strength with which they are tied up to the negative places on the colloidal micelle* (intensity factor). The affinity between the positive outer (H⁺) and negative inner layer (O⁻⁻, OH⁻, in Helmholtz's double layer) need not be constant for all colloidal aluminum silicates, since it obviously depends on the lattice arrangement of the negative ions in the colloidal complex. The ease of replacement of hydrogen ions which shall be called *avidity* (Truog)⁴⁹ varies considerably in different soils as pointed out by Parker.³⁹

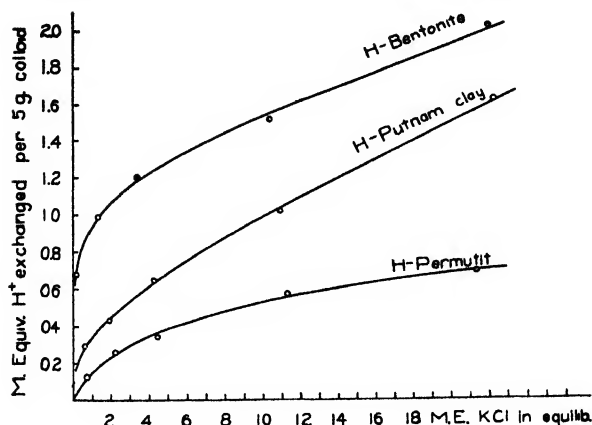


FIG. 5
Release of adsorbed hydrogen ions by KCl from various colloidal aluminum silicates.

In Table XIX the magnitude of avidity for three different aluminum silicates is expressed in various numerical terms. Irrespective of the formula

TABLE XIX

Avidity of Various Aluminum Silicates in the Exchange of H^+ against KCl

Numerical characterization	H-Permutit	H-Putnam clay	H-Bentonite
Constant k (Freundlich's isotherm)	5.94	12.05	15.22
Symmetry value	8.0%	15.0%	18.4%
Constant C (Vageler-Langmuir equation)	23.31	10.74	6.87
Apparent dissociation constant pK	7.28	5.97	5.67
Increase in avidity	→		

or mode of presentation used to characterize the intensity of the ionic exchange, it is clearly seen that all values increase from left to right. H-permutit has the smallest avidity and H-bentonite the greatest. According to Vageler's C -value 23.31 milliequivalents of KCl must be added to replace 50 per cent of the adsorbed H^+ from permutit, while only 6.87 milliequivalents are necessary to replace 50 per cent in the case of H-bentonite. If one adds the same amounts of K^+ ions as there are exchangeable H^+ ions on the colloids, only 8 per cent of the H^+ ions are replaced from the permutit, while 18.4 per cent are released from the bentonite (symmetry value). In other words, *the H-ions are held more tightly on permutits than on bentonites. Putnam clay occupies an intermediate position.*

In the same table figures are given for the "apparent dissociation constant." It has been calculated according to Bradfield,⁸ who accepts the

viewpoints of Loew, Ramann, Truog and others, and who considers clays as colloidal acids. He characterizes the nature of the mineral soil acids with the apparent dissociation constants based on the following equation:

$$\text{pH} = \text{pK} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Experimentally pK is determined by adding just enough base to the H-clay to neutralize one-half of the exchangeable H^+ ions. The resulting pH value corresponds to pK.

Naturally the dissociation constant and the avidity index must stand in close relation to each other since both are expressions for the affinity between the H-ion and the clay "anion." It is evident from Table XIX that on the basis of pK, H-permutit is a weaker acid than either H-Putnam clay or H-bentonite.

TABLE XX

Effect of Base and Time of Reaction on the Magnitude of the Apparent Dissociation Constant of Colloidal "Clay Acids"

(Based on pH measurements of sols)

"normality" = 0.0028 N

Base used for neutralization	Time of reaction	Permutit* $\times 10^{-7}$	Putnam clay $\times 10^{-7}$	Bentonite clay $\times 10^{-7}$
LiOH	4 days	0.141	5.02	8.91
	46 days	0.355	14.46	28.19
NaOH	4 days	0.224	5.62	12.60
	46 days	0.692	11.75	30.91
KOH	4 days	0.525	10.72	21.38
	46 days	1.203	30.20	70.80

* H-Permutit was ground in a mortar until it formed a relatively stable suspension.

Unfortunately the dissociation constant of colloidal clay acids is not of such great value as the dissociation constant of true weak acids. The trouble is that pK does not prove to be a constant; it varies enormously with the experimental methods used as seen in Table XX. From data of Bayer¹ it can be calculated that the dissociation constant for a 0.016 "normal" clay acid suspension varies 1900 per cent according to the base applied (LiOH, $\text{Ca}(\text{OH})_2$). It is also certain that pK varies with dilution, and furthermore it has a very great time factor. For these reasons the term "avidity index" instead of "dissociation constant" is used in order to avoid an impression of accuracy and consistency that does not exist.

The qualitative similarity between the avidity index and the dissociation constant leads to important suggestions regarding the release and adsorption of ions by colloidal aluminum silicates of various avidities, which demonstrates the heuristic value of the clay acid-viewpoint in ionic exchange.

a) *Release of H-ions.*

Under comparable conditions *weak clay acids release less H^+ than strong* clay acids*. This statement follows directly from the empirical definition of avidity. It has been tested by adding different salts to the H-colloids. Table XXI shows the relationship expressed in terms of symmetry values.

TABLE XXI

Release of H^+ from Electrodialyzed Colloidal Aluminum Silicates
(Symmetry values)

Substance added	H-Permutit	H-Putnam clay	H-Bentonite
$AgNO_3$	6.78%	7.91%	13.78%
KNO_3	—	11.30%	19.92%
KCl	8.0 %	13.0 %	18.4 %
NaCl	2.7 %	6.2 %	14.6 %
LiCl	1.0 %	6.7 %	18.0 %

It is evident that for all of the five different cations and two different anions used, more H-ions are replaced from the bentonite (stronger acid) than from the permutit (weaker acid). This shows that the differences in affinity existing between the various aluminum silicates and H-ions are independent of the salts used in the exchange experiments in this investigation.

On the basis of stoichiometrical replacement the corollary follows that a "*strong*"* *clay acid H-system adsorbs more cations than a weak clay acid*. This statement is of particular importance from the viewpoint of fertilizer applications to soils of humid regions which possess considerable amounts of exchangeable H-ions in their colloidal complexes.

b) *Adsorption of H-ions.*

Under comparable conditions *weak clay acids adsorb more H-ions than "strong" clay acids*. In other words, if HCl is added to basic clays, K-clays for instance, the aluminum silicate of lowest avidity will adsorb the most H-ions. In Table XXII the effect is shown quantitatively on the basis of symmetry values.

TABLE XXII

Adsorption of H^+ from HCl by Various Aluminum Silicates
(Symmetry values)
(From Tables III, IV, VII, XIII, XVI, XVIII)

System	Percentage of H adsorbed
NH_4 -permutit	83.58%
NH_4 -Putnam clay	74.82%
NH_4 -bentonite clay	60.90%
K-permutit	85.45%
K-Putnam clay	69.55%
K-bentonite clay	50.36%

* "Strong" in a relative meaning, as contrasted with "weak."

In every case permutit takes up the most H-ions and bentonite the least. If HCl is replaced by weak acids such as acetic acid, the effect still holds for Putnam clay and bentonite but is less conspicuous for permutits.

If the ionic exchange is stoichiometric the corollary follows that *adsorbed monovalent cations are more easily replaced (by H^+) from a weak clay acid than from a strong one.*

From the clay acid standpoint the entire problem of ionic exchange corresponds to the phenomenon of distribution of a base between two acids. If both acids are weak and their dissociation constants known, ionic exchange might be predicted quantitatively, as has been attempted by Bradfield. Since in this study only neutral salts of strong acids are brought into contact with clays the application of the above principle is excluded.

Summary of Discussion of Avidity of Soil Colloids.

1) Various colloidal aluminum silicates have different affinities for hydrogen ions. Bentonite has a high avidity, permutit a low one. Putnam clay takes an intermediate position.

2) From the clay-acid viewpoint, the avidity index can be related to the apparent dissociation constant of the clay acids. Putnam clay is a weaker acid than bentonite, while permutit is weaker than Putnam clay.

3) The following relations existing between ionic exchange and strength of clay acids have been suggested:

a) The weaker the clay acid the less H-ions will be released upon addition of a neutral salt.

b) The weaker the clay acid the less cations will be adsorbed by H-systems.

c) The weaker the clay acid the more H-ions will be adsorbed by basic systems.

d) The weaker the clay acid the easier are adsorbed cations replaced by H-ions.

Lytotropic Series and Exchange-Adsorption

The adsorption of monovalent cations by NH_4^- and H-colloids exhibits characteristic differences in the three types of aluminum silicates investigated. The various silicates will be discussed separately.

a) Permutit systems (artificial zeolites).

Fig. 6 and Tables II, III and IX, show that the intensity of ionic exchange is different for all cations studied. The individual behavior of the various ions is regularly manifested throughout the range of concentration used and can be expressed by various numerical values as indicated in Table XXIII.

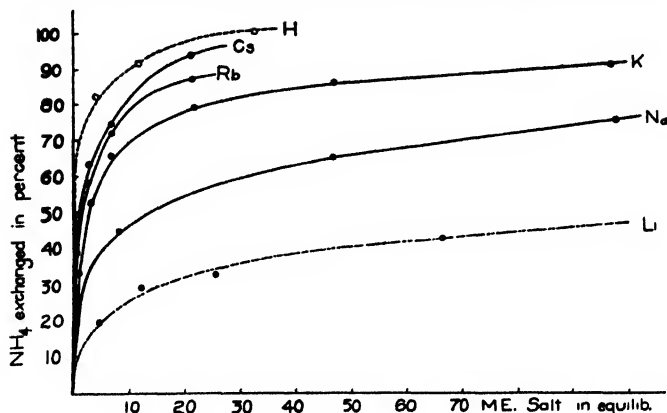


FIG. 6
Adsorption of cations by NH_4 -permutit.
(From Table II)

TABLE XXIII

Lyotropic Series as characterized by Various Numerical Values
(NH_4 -permutit + monovalent chlorides, equilibrium concentrations)

Salt added	Symmetry value	Wiegner-Freundlich isotherm		Vageler-Langmuir isotherm		Ganssen equation K
		$1/p$	$(1/p=0.57)$	S	C ($S = 4.15$)	
LiCl	16 5%	0.392	15.21	2 30	61.56	0.029
NaCl	32 5%	0.296	29.46	3 45	14.53	0.209
KCl	48.0%	0.226	45.07	3 88	6.46	0.715
RbCl	54 5%	0.226	56.75	4.07	2.09	1.947
CsCl	56 5%	0.296	57.98	4.31	1.44	2.421

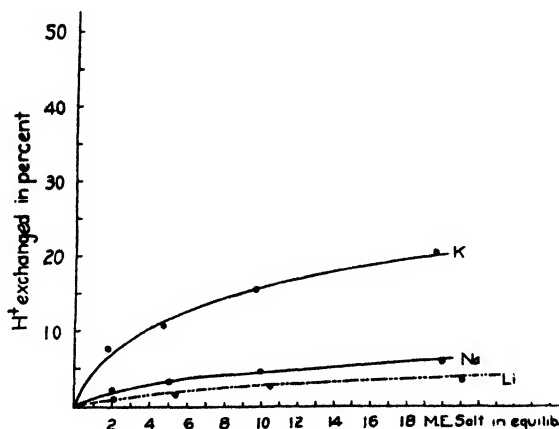


FIG. 7
Adsorption of cations from chlorides by H-permutit.
(From Table IX)

The magnitudes of all constants in the various equations clearly express a systematic trend in regard to the cation used. Whether the formula is based on strictly chemical principles (law of mass action) or whether it designates physical adsorption, the lyotropic series is always manifested. The above type of comparison is valid for all systems studied. For the sake of simplicity and uniformity the symmetry value will be mainly used for the quantitative characterization of the exchange intensity of the various cations.

The lyotropic series is independent of concentration and is noticeable in pure NH_4 -systems, in pure H-systems (Fig 7) or in mixtures of NH_4 -H-systems, as illustrated in Table XXIV.

TABLE XXIV
Adsorption of Monovalent Cations by Various Permutit Systems
(Symmetry Values)

System	Li	Na	K	Rb	Cs	H
	%	%	%	%	%	%
NH_4 -permutit (Table II)	16.5	32.5	48.0	54.5	56.5	—
NH_4 -H-permutit (Table III)	16.0	33.5	44.0	—	—	83.6
pH range	7.0-7.1	6.9-7.1	6.8-7.5	—	—	2.4-6.5
H-permutit (Table IX)	1.0	2.7	8.0	—	—	—
pH range	4.9-5.0	4.75	4.60	—	—	—

Although H-permutit adsorbs fewer cations than NH_4 -permutit, the lyotropic series is noticeable in every case, both under alkaline and acid conditions. For all permutit systems the lyotropic series assumes the following form in regard to adsorption:



Li is least adsorbed and H is best adsorbed. The differences are very great, amounting to 240 per cent between Li and Cs in NH_4 -permutit and 700 per cent between Li and K in H-permutit.

b) Putnam clay-systems.

Tables IV, V, VI and X and Figs. 8, 9 and 10 give information as to the existence of the lyotropic series in the natural soil colloid, Putnam clay. Again pure NH_4 - and H- and combined NH_4 -H-clay systems were studied. A glance at the various graphs reveals at once that the lyotropic series is clearly manifested, but at the same time one may notice a significant difference in the case of Li and Na. Both curves are closely associated. In dilute concentrations Li is slightly better adsorbed than Na, while at higher concentration it is somewhat less attracted. Table XXV expresses the adsorption intensity on the basis of symmetry values.

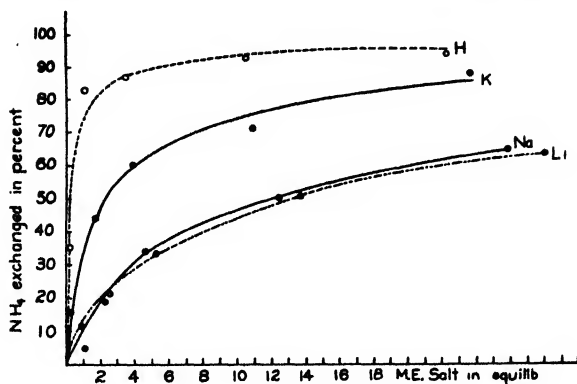


FIG. 8
Adsorption of cations by $\text{NH}_4\text{-H}$ -Putnam clay.
(From Table IV)

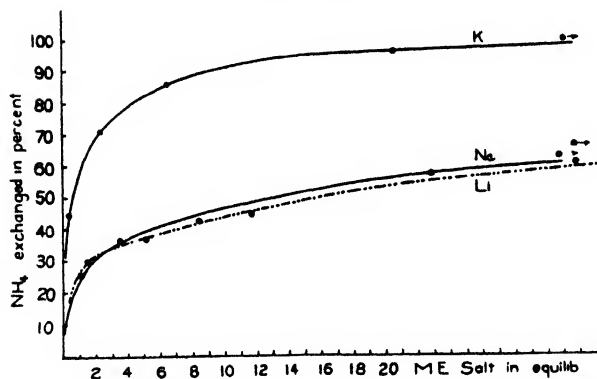


FIG. 9
Adsorption of cations by NH_4 -Putnam clay.
(From Table V)

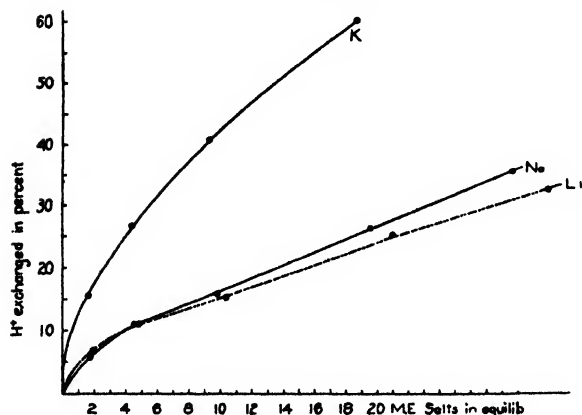


FIG. 10
Adsorption of cations by H-Putnam clay.
(From Table X)

TABLE XXV

Adsorption of Monovalent Cations by Various Putnam Clay Colloids
(Symmetry Values)

System	Li	Na	K	H
NH ₄ -Putnam clay (Table V)	31.5%	32.8%	63.7%	—
pH of sol at equilibrium	7.24	7.04	8.00	—
NH ₄ -H-Putnam clay (Table IV)	37.5%	35.7%	54.0%	83.0%
pH of sol at equilibrium	5.26	5.23	5.05	4.15
NH ₄ -H-surface soil (Table VI)	33.2%	35.8%	55.0%	63.8%
pH at equilibrium	5.31	5.22	4.88	3.10
H-Putnam clay (Table X)	6.7%	6.2%	13.0%	—
pH at equilibrium: sol	3.91	3.93	3.72	
Intermicellar liquid	4.05	3.93	3.67	
H-Sharkey clay (Table XII)	9.0%	10.4%	15.2%	

For all five systems the symmetry values express quantitatively the adsorption similarity of Li and Na. In natural clays and soils the lyotropic series is also independent of the nature of the adsorbed ion, concentration of salt added and acidity or alkalinity of the system. In fact, every cation brings the sol to a pH value characteristic for the added ion. The order of the ions in the lyotropic series must be written as follows:

$$\text{Li} = \text{Na} < \text{K} < \text{H}$$

Experiments conducted with colloidal clay extracted from a river bottom soil known as Sharkey clay yielded a similar series as shown in Table XXV.

c) *Bentonite clay systems.*

Tables VII, VIII, XI and Figs. 11 and 12 give information about cation adsorption in natural bentonite clays from Wyoming. Certain peculiarities are striking. In all systems the curves are closer together than either in Putnam clays or permutits. Such is especially the case for the NH₄-H-bentonite series. The Li-curve is especially interesting. In dilute concentrations Li is better adsorbed than Na, it approaches the intake of K and even exceeds it in the case of NH₄-H-bentonite. In higher concentrations the behavior of the cation is more similar to the Putnam clay systems, especially in the case of H-bentonite. None of the formulae proposed is able to describe satisfactorily the irregularities within the family of the curves. Characterization of the adsorption intensity by symmetry values gives the following data (Table XXVI).

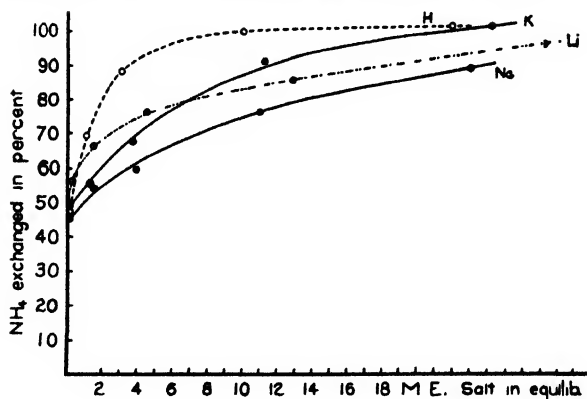


FIG. 11
Adsorption of cations by NH₄-H-Bentonite.
(From Table VII)

TABLE XXVI

Adsorption of Monovalent Cations by Bentonite Clay Systems
(Symmetry Values)
(From Tables VII, XI)

System	Li	Na	K	H
NH ₄ -H-bentonite clay	60.5%	50.6%	53.0%	60.90%
pH of sol at equilibrium	6.12	5.82	5.89	4.30
H-bentonite clay	18.0%	14.6%	18.4%	—
pH of sol at equilibrium	2.98	3.06	2.87	—

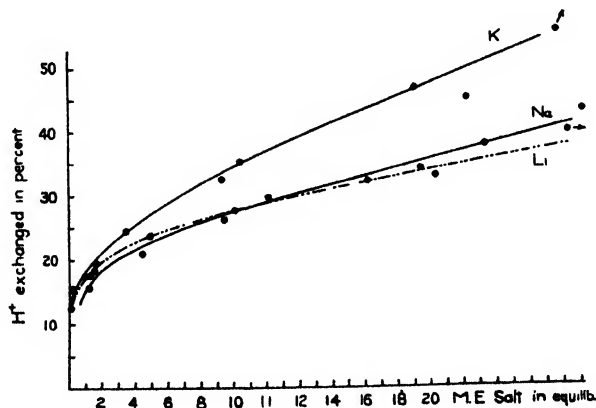


FIG. 12
Adsorption of cations by H-Bentonite.
(From Table XI)

Although the absolute intensity of exchange is different in the two systems, the abnormal position of Li is clearly manifested. The symmetry value of Li is close to that of K and even exceeds it in the $\text{NH}_4\text{-H}$ -system. Two experiments conducted at alkaline reactions (pH of $\text{NH}_4\text{-sol}=8.5$) gave very similar results. Comparisons on the basis of Vageler's C-value, calculated for comparable concentrations (5-12 milliequivalents of salt) are shown in Table XXVII.

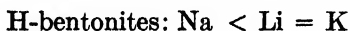
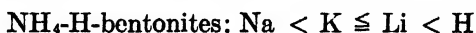
TABLE XXVII

Adsorption of Li, Na, K by $\text{NH}_4\text{-}$ and $\text{NH}_4\text{-H}$ -bentonite Colloids
(Vageler's C-values)
(From Tables VII, VIII)

System	Li	Na	K
$\text{NH}_4\text{-bentonite}$ clay, alkaline reaction	2.30	2.78	1.65
$\text{NH}_4\text{-H-bentonite}$ clay, acid reaction (Same system as in Table XXVI)	1.77	3.59	1.25

The numbers indicate the milliequivalents of salt that must be added in order to replace 50 per cent of the exchangeable NH_4 . Again Li approaches the effectiveness of Na and K.

For dilute concentrations and on the basis of symmetry values the lyotropic series assumes the following form:



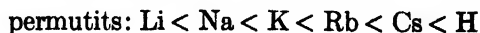
Generally speaking all curves lie closer to the H-curve than in the case of the previous systems.

d) *Summary of the adsorption of monovalent cations.*

1) The lyotropic series representing the individual behavior of cations is manifest in all systems studied.

2) The presence of the series is independent of the strength of clay acid, acidity or alkalinity of the system, concentration range, temperature, time of reaction, size of colloidal particle, etc.

3) The various colloids exhibit characteristic differences in the position of the elements in the series. In dilute to moderate concentrations the order in the $\text{NH}_4\text{-systems}$ is as follows:



Lithium is the most affected ion. It gradually shifts from the lowest position in permutits to nearly the highest in bentonites. At very high concentrations the lyotropic series becomes less accentuated.

Release of Ions and Lyotropic Series

In the discussion on adsorption the fact has been stressed that the various cations exhibit characteristic individualities in regard to their adsorbability. It would be of great interest to learn whether the adsorbed ions retain their individuality after they have "settled down" on the surface of the colloidal particles. There are various methods which would permit more or less satisfactory answers to this question, for instance, the study of hydration of clays, viscosity, cataphoresis and so forth. In this paper, interest will be concentrated around the *outgo* or release of adsorbed cations and its relation to the lyotropic series. In order to obtain quantitative information it is necessary to prepare under strictly comparable conditions, a series of clays which contain but one kind of exchangeable cation, for example Li or Na or K. This was done by leaching clays with neutral salts or by adding hydroxides to H-clays.

a) Release of adsorbed ions from permutit systems.

The outgo of adsorbed ions was studied by treating Li, Na, K, NH_4 , and H-permutits with various amounts of NH_4Cl or HCl. Fig. 13 and Table XXVIII, which express the intensity of exchange in terms of symmetry values, illustrate quantitatively that the cations behave individually in their outgo as well as in their intake.

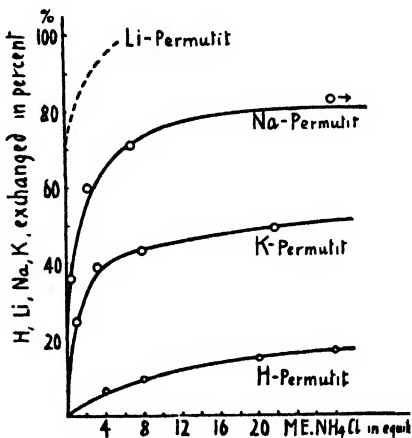


FIG. 13
Release of adsorbed Li, Na, K, and H from permutits by NH_4Cl .

TABLE XXVIII

Release of Adsorbed Ions from Permutits. (Symmetry Values)
(From Table XVIII and Jenny²⁴)

System	Release against NH_4^+	Release against H^+	
		System I	System II
Li-permutit	70%	82.05%	—
Na-permutit	55.0%	77.40%	89.98%
K-permutit	37.5%	73.20%	85.45%
H-permutit	5.46%	—	—

Although the absolute values differ in the two columns because the H-ion is a much more energetic replacing agent than the NH_4 -ion, it is clearly seen that in both cases Li is much easier released than either Na or K. The release of adsorbed cations is just in the reverse order to their adsorbability, and the lyotropic series can be written as follows:

Release: $\text{Li} > \text{Na} > \text{K} > \text{H}$

The outgo of the various cations was determined by analyzing the replacing NH_4Cl and HCl solutions before and after the experiment.

b) *Release of adsorbed ions from Putnam clay systems.*

The "basic clays" were prepared by adding just enough hydroxide to electrodyalized clays to neutralize quantitatively all exchangeable H-ions. The number of exchangeable H-ions on the colloid was determined by continuous leaching with KCl and titration of the resulting HCl as described in a previous chapter. Figs. 14 and 15, and Table XXIX express the relationship between outgo of bases and intake of NH_4 and H quantitatively.

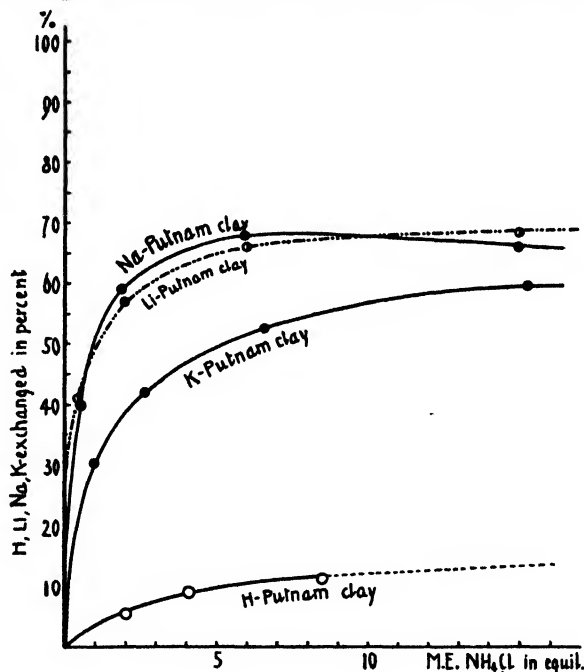


FIG. 14
Release of adsorbed Li, Na, K, and H from Putnam clays by NH_4Cl .
(From Table XIV)

TABLE XXIX

Release of adsorbed cations from Putnam clays
(Symmetry Values)

System	Released against NH_4Cl from Table XIV	Released against HCl	
		(old sol) from Table XIII	(young sol) from Table XVII
Li-Putnam clay	57.08%	78.70%	84.48%
Na-Putnam clay	58.90%	80.30%	86.10%
K-Putnam clay	42.03%	69.55%	80.90%
H-Putnam clay	6.90%	—	—

Generally speaking, the picture is the same as that for permutits. Again HCl displaces much larger amounts of adsorbed cations than NH_4Cl , but in

both sets of experiments the order of release of adsorbed ions is consistent. The lyotropic series reads as follows:

Release: $\text{Li} = \text{Na} > \text{K} > \text{H}$

Li and Na are close together, the former being held slightly tighter than the latter in moderate concentrations. Remembering the order of the lyotropic series found for the adsorption of cations by Putnam clay, it is evident that the outgo is just the reverse of the intake.

Table XXIX also indicates the presence of a *hysteresis* phenomenon. Freshly prepared, young (one week old) basic clays have higher symmetry values than older sols in which HCl was added six months after the Li-, Na-, K-clays had been prepared. In young sols the ions apparently are less firmly bound by the colloid than in older sols. In other words, it seems that ageing renders the liberation of adsorbed ions more difficult.

c) *Release of adsorbed ions from bentonite clays.*

The bentonite "basic clays" were prepared similarly to the Putnam clays. The results of the two systems are exactly comparable since the transformation of the H-systems into salt systems and the subsequent ionic exchange experiments were always run in parallel. This is of importance because of possible disturbances due to the observed hysteresis phenomenon. Figs. 16 and 17 and Table XXX explain the release of Li, Na, K, NH_4 and H against NH_4Cl and HCl.

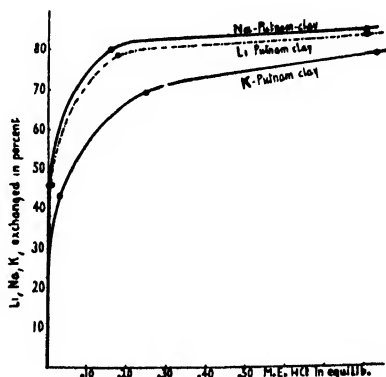


FIG. 15

Release of Li, Na, and K against HCl from Putnam clay. (From Table XIII)

TABLE XXX

Release of Adsorbed Ions from Bentonite Clays
(Symmetry Values)

System	Release against NH_4^+ From Table XV	Release against H^+	
		(old sol) From Table XVI	(young sol) From Table XVII
Li-bentonite clay	46.52%	59.83%	77.90%
Na-bentonite clay	49.59%	60.40%	76.41%
K-bentonite clay	43.75%	50.36%	74.12%
H-bentonite clay	14.45%	—	—

The data for the bentonite clays confirm the observations made in the other systems. Again H^+ replaces more cations than NH_4^+ , but the lyotropic series remains consistent. The ageing effect is also noticeable, the availability of Li, for instance, decreased 23 per cent in six months.

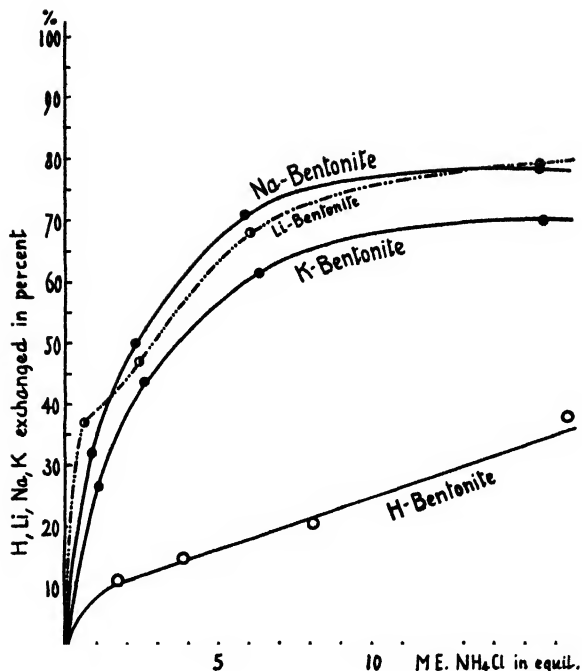


FIG. 16
Release of adsorbed Li, Na, K, and H from Bentonites by NH₄Cl.
(From Table XV)

The order of the elements in the lyotropic series reads as follows:

$$\text{Release: Li} \begin{matrix} \cong \\ < \end{matrix} \text{Na} > \text{K} > \text{H}$$

There exists a slight difference between the intake and outgo of cations in bentonite systems. According to symmetry values Li stands closer to K in the adsorption series, while in release it acts more like Na. However, a glance at the adsorption curves in Fig. 11 shows that in higher concentrations Li behaves in the intake more like Na than K. As pointed out in the chapter on mathematical formulation it is very difficult to characterize the irregular behavior of the Li ion in bentonite systems with a single value. Generally speaking, the lyotropic series is somewhat less marked in bentonite than either in Putnam clay or permutit. It is of considerable interest to note that in dilute NH₄Cl concentration the adsorbed ions Li, Na, K are more strongly held on Putnam clay particles (weaker clay acid) than on the bentonite colloid, while under high NH₄Cl concentrations the reverse is true.

d) *Summary on release of monovalent cations.*

1) The adsorbed ions retain their individuality in their release from the colloid.

2) Generally speaking, the order of the ions in the lyotropic series during release is the reverse of the order during adsorption.

The Explanation of the Lyotropic Series encountered in Ionic Exchange

After it has been established that the cations behave individually during ionic exchange, both in intake and outgo, it would be of interest to learn more about the underlying causes of the lyotropic series observed. Can the constants of the equations or the symmetry values be correlated with ionic properties and is it possible to throw some light on the shifting of the ions within the Hofmeister series? Not only would a satisfactory answer be significant for clay studies, but also from the viewpoint of general colloid chemistry, since the lyotropic series and their irregularities have been observed in numerous other colloidal systems.

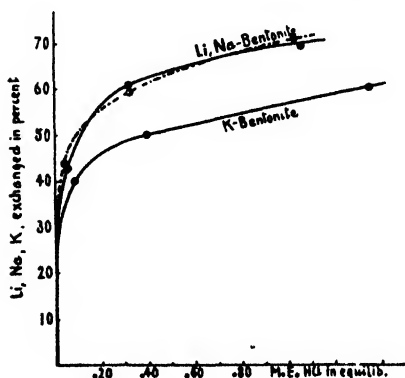


FIG. 17

Release of Li, Na, and K against HCl from Bentonite. (From Table XVI)

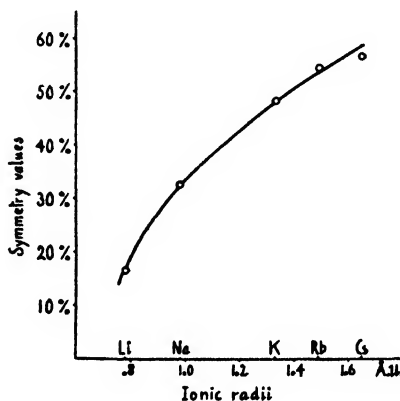


FIG. 18

Adsorption of cations by NH_4 -permutit in relation to ionic radii.

a) The normal series in NH_4 -permutit-systems.

The intake of cations by NH_4 -permutit proceeds according to the following series:



In order to be able to visualize the ionic exchange these symbols of cations must be replaced by measurable properties of the ions. A glance at the periodic system reveals that the ions in the lyotropic series are arranged according to their atomic weights. From the viewpoint of surface mechanics, however, atomic weight is less instructive than other properties, such as electric charge and size of ions, since these permit calculations of attraction and space relationships. Since all cations investigated in this study are of identical charge, the ionic exchange intensities, expressed as symmetry values, can be directly related to the size of the ions. This has been done in Fig. 18. It is clearly seen that the *symmetry values are greater the larger the radius of the cation*. The relation is not quite linear. The resulting curve is slightly convex showing that a straight line relation is found (except for Cs) if the symmetry values are plotted against the logarithms of the ionic radii. Apparently there exists a distinct *space relationship* in ionic exchange reactions. The colloid particle seems to prefer ions of large size. From the viewpoint

of *energy relationships* the size of ions and their charge must be combined. In calculations of molecular energy and crystal lattice energy the electrostatic potential of the ions plays a very important rôle. Since the crystal structure of the colloidal exchange complex does not alter during ionic exchange, as revealed independently by microscopical and by X-ray analyses, the electric field of the active places on the crystal-surface remains constant; it is permissible, therefore, to relate the intensity of ionic exchange expressed as symmetry values directly to the potential of the exchanging cation. Fig. 19 illustrates that adsorption is better the smaller the electrostatic potential of the cation. Very similar curves are obtained if the constants of the Wiegner-Freundlich isotherm are correlated with radii and potential.*

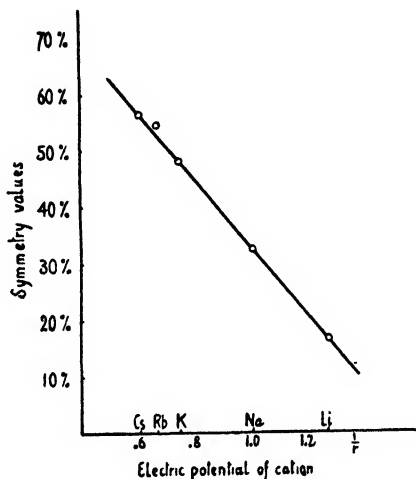


FIG. 19

Adsorption of cations by NH_4 -permutit in relation to electric potential.

These findings are not only interesting but also puzzling. They are interesting because the observed relationships give the lyotropic series in ionic exchange a physical meaning which can be expressed numerically. On the other hand, the results are puzzling because they are directly opposite to what one would expect from analogies of attraction and energy relations in crystal lattices. According to Born,³ Kossel,³¹ Goldschmidt²¹ and others,⁴¹ the attraction between anions and cations in ionic crystals, obeys *Coulomb's law* which demands that for cations of equal charge a small ion (Li) be attracted with greater force and held more tightly than a large ion (K, Cs). Symmetry values should decrease with increasing ionic radii and increase with electric potential. Strangely enough, they exhibit a reverse relationship.

The colloidal aluminum silicates belong to the polar ionic crystal compounds as pointed out in the chapter on the nature of the colloidal complex.

* In previous work²⁴ it was found that the constants k of the Wiegner-Freundlich equation are directly proportional to the true ionic volume of the exchanging cations. Although this result is highly significant from the standpoint of the energy of hydration, it should be pointed out that this relation had been obtained on the basis of the old ionic radii of Bragg, which, according to Wasastjerna, are somewhat too great.

The electrostatic bond conception can, therefore, be applied to the ionic exchange reactions in permutits. The active places of attraction for the cations are O^{--} ions and probably also OH^- ions on the surface of the colloidal particle. These two anions differ mainly in their strength of attraction for cations. The sizes are almost alike, but on account of the double electric charge the oxygen anions are more powerful "adsorbents." They form the negative inner layer of the Helmholtz double layer. A force of attraction (and, of course, also Born's repulsion) exists between an isolated surface anion and the adsorbed cation which is equal to $\frac{e_a \cdot e_c}{(r_a + r_c)^2}$ where e_a , e_c are the charges and r_a , r_c are the radii of the cation and anions respectively. The energy liberated at equilibrium is expressed as $\frac{e^2}{r_a + r_c}$ if cation and anion are monovalent. The energy of formation of such an ionic molecule is a measure of the stability of the compound. It is evident from the radius sum in the denominator that *attraction and stability are greater the smaller the radii of the ions*. For a constant anion the molecular energy varies for different cations as follows:



If the ions are deformable the above energy equation must contain an additional term which expresses the energy gained due to the electric polarization effect. For ions within a polar crystal the polarization effect is small and the crystal energy can be calculated on the basis of mere Coulomb attraction, if the so-called Madelung constant for the lattice is known. Adsorption compounds on the surface of crystals and colloidal complexes such as the aluminum silicate particles take an intermediate position between single ionic molecules and large lattice molecules. The surface ions are not symmetrically surrounded by electric charges of opposite sign. The coordination number of surface ions is likely to be less than that of interior ions and consequently the ionic radii will become somewhat smaller. In attempting to calculate ionic exchange energies on colloidal aluminum silicates, it would be necessary to consider the polarization of the deformable surface oxygen anion in the presence of exchangeable cations. Such detailed calculations have not yet been made.

The results found in this investigation show that *in ionic exchange the cations apparently act contrary to Coulomb's law*. The small Li ion is least adsorbed and most easily released, while the large K ion is strongly attracted and difficultly replaced. The effect of the interionic distance is reversed.

In searching for a possible explanation of this phenomenon, the relation between symmetry values and ionic potential recalls the formula for the migration velocity of ions as based on Stokes law which also contains the expression e/r . The velocity of large ions is directly proportional to their potential, but for the monovalent cations Li to Cs the relation is a reverse one, as is the case for their adsorption by permutits. The large Cs and K ions migrate faster than the small Li and Na ions. In other words, there

exists a striking similarity between adsorption and migration velocity of ions which can be formulated as follows: *the adsorption of monovalent cations is better the greater their mobility*, a conclusion which was postulated on theoretical reasoning by Mukherjee⁸⁶ several years ago.

It seems logical to attribute the order of the lyotropic series in adsorption and release in permutits to the same cause as that of the mobility of ions, namely, to the phenomenon of *hydration of ions*.

As soon as Arrhenius had postulated the theory of dissociation, the hypothesis that the ions interact with the surrounding water molecules was put forward by numerous eminent investigators (Arrhenius, Kohlrausch, Nernst, Drucker, Washburn). Recently the hydration of ions has been attacked by theoretical physicists (Fajans, Born, Debye, Webb, Lange) by the application of rigorous mathematical treatments. Their calculations are mainly based upon the following picture: The interaction of ions and water molecules is not a chemical, stoichiometrical one, but is essentially an electrostatic phenomenon. The electric field intensity ($e:r^2$) in the vicinity of an ion is very great, for instance, 180,000 volts per cm. at a distance of 10^{-7} cm. from the center of a sodium ion. Water molecules, which are permanent dipoles, become oriented and attracted, turning their negative side toward the cation. The number of polarized water molecules increases with the polarizing ability of the ion which is stronger the greater its charge and the smaller its radius. The small Li ion will, therefore, attract the most water molecules and the large Cs ion the least. Li will then be the largest ion and Cs the smallest. Hydration and mobility radii will, therefore, decrease according to the series:



This is exactly the same order as the one found in adsorption by NH_4 -permutits. The presence of water shells around ions also has been indicated by X-ray analyses of salt solutions.⁴⁴

With the aid of the concept of hydration of ions, the mechanism of ionic exchange in permutits is easily visualized. The strongly hydrated, large and voluminous Li-ion cannot come very close to the negative oxygen ion of the crystal lattice, since there are one or two water molecules between the colloidal particle and the adsorbed cation. The forces of attraction are, therefore, weak because they vary inversely with the square of the distance between the electric charges (Coulomb's law). Adsorbed Li-ions are, therefore, easily replaced by less hydrated and consequently smaller ions, such as K, Rb, Cs, which are very strongly attracted by the negative places in the crystal lattice. They stick there tightly because the effective interionic distance is relatively small. Adsorbed slightly hydrated cations are replaced with difficulty particularly if the exchange is brought about by strongly hydrated ions such as Na and Li. On the basis of the hydration of ions the ionic exchange in permutits can be expected to take place as follows:

Adsorption: $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$

Release: $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

which is exactly the lyotropic series observed.

The possible connection between ionic exchange in permutits and hydration of ions was first suggested by Wiegner.⁵⁶

The observed contradiction between the electrostatic attraction of ions in crystals and in base exchange reactions on colloidal aluminum silicates is, therefore, only an apparent one. Coulomb's physical law can explain the behavior of the ions in both systems. The main difference is the following: in calculating the forces of attraction and the resulting energies according to the formulae given, the ionic radii of Goldschmidt and Pauling have to

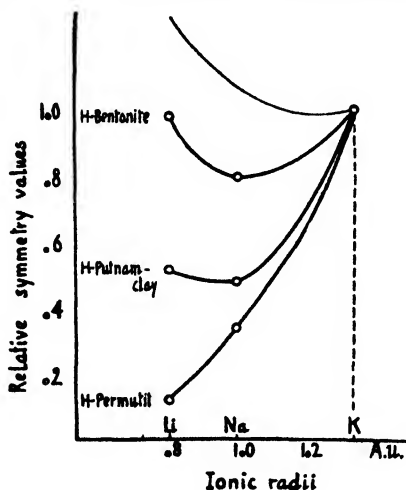


FIG. 20

Relative ionic exchange intensities as a function of ionic radii and nature of colloidal aluminum silicate.

be used for crystals, while for ionic exchange reactions on the surface of the colloid the radii of the hydrated ions (electrodynamic radii) must be inserted. The latter vary much more than the former.

b) *The disturbed lyotropic series in Putnam clay and bentonite systems.*

The normal lyotropic series encountered in NH_4 -permutits is distinctly disturbed in Putnam clay and bentonite systems. In dilute and moderate concentrations the natural aluminum silicates adsorb relatively more Na and Li than K. For a quantitative comparison of the different lyotropic series it is best to reduce the symmetry values to *relative* exchange intensities. This has been done for the H-colloids in Fig. 20, by placing the symmetry value of K^+ equal to one. This procedure reveals at once a certain regularity in the disturbance of the various lyotropic series of the natural clay systems. It will be noticed that the H-permutit curve (lowest curve) exhibits a slightly concave bending. The bending is intensified in the H-Putnam clay curve and becomes most conspicuous in the H-bentonite system where a pronounced minimum is clearly noticeable. The impression is gained as if a pull is being exerted on the Li end of the curve in the direction of higher relative symmetry values. There exists a marked tendency to reverse the normal lyotropic

series. A very similar picture can be obtained by plotting the relative symmetry values of the various Li-, Na-, K- and NH_4 -systems. In NH_4 -H-bentonite Li already lies higher than K. It could be easily conceived that there might exist a system in which the order of Li, Na, K is completely reversed as indicated by a thin line in Fig. 20. Temperature experiments demonstrate that the difference in exchange intensities between K and Na becomes smaller as the temperature increases. Indeed, Jaeger's experiments with Ag-ultramarines conducted at temperatures of 160°C , show that the lyotropic series is reversed. Jaeger²³ says, "The substitution of the Ag present, under equal conditions of temperature, concentration and time of heating (in sealed tubes) goes most rapidly and completely with Li and less rapidly with Na, K, Rb, Cs in decreasing ratio; the substitution of NH_4 is almost the same as that of K."

The observed irregularities in the lyotropic series of natural aluminum silicates can be interpreted as *various stages in the reversal of the normal hydration order of the exchanging cations*. This conclusion may also shed new light upon the behavior of ions in other colloidal systems where similar abnormalities are frequently encountered.

From the viewpoint of hydration of ions it is logical to connect the reversal of the lyotropic series with dehydration of ions. Obviously the most hydrated ion will be first affected by dehydration processes. This is demonstrated by the behavior of the Li-ion which is the first to begin shifting within the series. In bentonite and clay systems, for example, Li appears to be so strongly dehydrated that it becomes as active as Na. The fact that the cations may also act as dehydrated ions in ionic exchange was shown by Souviron⁵⁷ who studied adsorption in alcoholic solutions, and later by Ungerer who observed a dehydrating effect of the anion upon the cation.

c) *The effective size of ions in exchange reactions.*

The consideration of ionic radii sheds considerable light on the mechanism of ionic exchange. It becomes necessary, however, to attribute various sizes or spheres of influence to the same cation depending on the nature of the collidal system in which the reaction takes place. The following extreme cases are important:

- a) crystal lattice radii (dehydrated ions);
- b) hydrodynamic radii (hydrated ions).

Crystal lattice radii refer to completely dehydrated ions as found in crystals (NaCl , CaO , many silicates). The radii increase with atomic weight, from Li to Cs (see Table XXXI), and vary slightly with the coordination number.

TABLE XXXI

Ionic Radii (Spheres of Action) of Hydrated and Dehydrated Ions
(Ångstrom units)

	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+
Crystal lattice radii	0.78	0.98	1.33	1.43	1.49	1.65
Hydrodynamic radii	10.03	7.90	5.32	5.37	5.09	5.05

The *hydrodynamic radii* represent the sizes of hydrated ions as found in solutions. They include the size of the ion proper and its water shell. These somewhat hypothetical radii vary considerably with concentration and are also affected by temperature. Table XXXI shows the hydrodynamic radii for ions in infinite dilution where hydration probably reaches a maximum. Although these radii are subject to revision they, nevertheless, demonstrate two significant things. First, the hydrodynamic radii are greater than the crystal lattice radii, and secondly the order of the element in the series is reversed. Crystal lattice ions increase from Li to Cs, while the hydrodynamic radii decrease. In colloidal systems containing kinetically mobile water molecules the effective size of a cation will have a value lying between the extremes listed in Table XXXI. For instance, Li may have an effective ionic radius greater, equal, or smaller than K, depending upon the conditions of hydration in the colloidal system. In permutits, at room temperature, fixation of cations takes place according to Coulomb's law on the basis of hydrodynamic radii, while in ultramarines at high temperature, ionic exchange proceeds according to crystal lattice radii. At present it is not yet possible to state a priori the nature of the effective sizes of ions in exchange reactions for any particular colloidal system.

The Peculiar Behavior of the Hydrogen Ion in Ionic Exchange

In the discussion of the mechanism of cation exchange the hydrogen ion was not mentioned. Owing to its great practical significance in the problem of soil acidity and on account of its peculiar behavior in adsorption and release, a separate consideration of the hydrogen ion becomes desirable.

In all systems investigated the hydrogen ion is unquestionably the best adsorbed ion. It is also most effective in replacing other cations from the surface of colloidal particles. Figs. 6, 8, 11 and the symmetry values in Tables XXIV-XXVI show that, independent of the avidity of the clay acid, the hydrogen ion curve is above the other curves, and that even in moderate concentrations it replaces almost completely all exchangeable monovalent cations. As to its release or exchangeability, the H-ion is most difficult to replace (Figs. 13, 14, 16); it sticks tenaciously to the colloidal particle. Unless the electrolyte added is able to bind the liberated H^+ —as is the case with hydroxides—complete exchange with one salt treatment is hardly achievable.

This unique position of the H-ion in the lyotropic series was pointed out in earlier studies²⁴ and has since been confirmed by numerous investigators, especially by Kappen.²⁶ The results serve to bring out the omnipotence of the hydrogen ion in many important soil processes. It is the hydrogen ion that first replaces the cations in the crystal lattice of silicates thus initiating the chemical weathering process which ultimately leads to the formation of soil and soil colloids. It is the H-ion (excreted) also which enables plants and microbes to liberate adsorbed cations which are necessary for growth. On the other hand, since the hydrogen ion is the least affected ion in leaching processes of soils, it adheres so tenaciously to the soil colloids and accumulates in such vast amounts that it becomes a serious menace to the agriculture of

humid regions. The American farmer annually applies thousands of tons of limestone to the soil in order to liberate and neutralize adsorbed hydrogen ions for the benefit of his crops.

From the viewpoint of the ionic exchange mechanism, the behavior of the H-ion is particularly interesting. The hydrogen ion consists of only a positive nucleus and is the smallest ion known. From analogy of Fig. 18 which shows that adsorption is directly proportional to size, the H-ion should be the least adsorbed cation. Contrary to this the H-ion is the most strongly adsorbed ion, exceeding the heavy elements Rb and Cs. On the basis of ionic size, H^+ acts even much more energetically than an H_2O -ion, which often is considered to be the adequate formula for the H-ion. The conditions are similar to those encountered in the migration velocity of ions where H exceeds by far any other cation.

The strong adsorption and difficult release of H-ions is perhaps better understood from a consideration of the forces of attraction. As mentioned before, the bonds existing between the oxygen ion frame and the adsorbed cations are considered to be of mere electrostatic nature (Coulomb attraction). There naturally exists for the adsorbed H-ions the tendency to form OH-ions and even H_2O molecules with O^{--} ions of the crystal lattice. The attraction between O^{--} and H^+ is very great. According to Debye¹⁸ the two ions adhere so closely that the H-ion even plunges into the electron orbits of the oxygen ion. Fajans¹⁷ emphasizes the great distortion of the oxygen ion due to the polarization of the H-ion. Pauling¹⁸ approaches the "compound" from quantum mechanics and considers the bond to be of covalent type, the two ions sharing two electrons simultaneously. This latter covalent or homopolar bond represents true chemical linkage most closely.

It seems, therefore, possible to trace the action of the H-ion back to significant differences in the type of bonds between the cation and the anion. In the case of Li and Na where it is probable that at least one water molecule stands between the O^{--} and the cation the attraction is weak and of an electrostatic type, while in the case of H^+ the forces are strong and seem to be of a true chemical type. This difference may also explain why those investigators who work mainly with H-systems emphasize the chemical nature of "clay acids," while those who study ionic exchange with cations other than H^+ stress the electrostatic and physical aspect more strongly. In all cases, however, the ionic exchange has to be stoichiometrical in order to satisfy the requirements of electrical neutrality.

The Hydration of Colloidal Particles as affected by Ionic Exchange

Investigations on the water adsorption of soil colloids by various methods show decidedly that the hydration of the colloidal particles depends upon the nature of the adsorbed cation. According to previous studies²⁴ the water content of wet permutits varies as follows:

Li-permutit	Na-permutit	K-permutit	H-permutit
60.64% H_2O	57.50% H_2O	53.48% H_2O	71.60% H_2O

The water content of the permutit is greater the more hydrated the adsorbed cation. Curiously enough the H-permutit contains the most water, although the hydrogen ion behaves as a dehydrated ion during exchange. The pronounced hydration of the H-systems has been confirmed by other methods and investigators as seen from the following figures, based on molecular values:

Transformation of NH_4 -permutit into H-permutit by leaching with dilute HCl (Jenny).²⁴

	SiO_2	Al_2O_3	$(\text{NH}_4)_2\text{O}$	H_2O
NH_4 -permutit	3.32	1	0.86	3.82
↓				
H-permutit	7.41	1	0	14.39

Transformation of Na-permutit into H-permutit by electrodialyses (Kappen).²⁶

	SiO_2	Al_2O_3	Na_2O	H_2O
Na-permutit	3.20	1	1.00	4.66
↓				
H-Na-permutit	3.30	1	0.55	6.56

No one has attempted to explain this abnormality between slightly hydrated H-ions and strongly hydrated H-colloids, which—as Kappen points out—presents a serious handicap for a complete understanding of ionic exchange. However, on the basis of the work presented it seems possible to suggest a general mechanism for the hydration of soil colloids which explains—at least qualitatively—the relation between water adsorption and ionic exchange in macroscopic permutit grains.

Permutit gels contain large cavities (see Fig. 3), which are filled with adsorbed (wandering) ions and water molecules. For a given crystal lattice the number of water molecules which can be packed into one cavity apparently depends upon the number and size of the exchangeable ions within the cavity. *The smaller the number and the true* size of the adsorbed ions, the greater will be the number of water molecules in the system.* Upon this simple picture the following possibilities can be set forward:

1) *Monovalent systems:* Under ordinary experimental conditions ionic exchange in permutits is stoichiometrical. For every monovalent cation adsorbed one other monovalent cation is released. Obviously the number of water molecules within the cavities becomes dependent only upon the size of the adsorbed cation. The smaller the exchangeable cation in the the cavity, the greater the number of water molecules that can be packed into the system. The hydration of monovalent permutits should, therefore, vary according to the following series:

$\text{Li-permutit} > \text{Na-permutit} > \text{K-permutit}$, etc.

Experiments previously cited show that this series actually exists.

2) *Divalent systems:* For exchange with divalent cations the ionic replacement in permutits was also found to be stoichiometrical. For every divalent cation adsorbed, two monovalent cations are liberated. From the viewpoint of space relations a highly interesting situation arises. Although the entire

* Crystal lattice radii.

system remains electrically balanced, yet the place of one of the two cations remains unoccupied, since the divalent cation certainly is not split up into two parts. For instance, the volume of two Na-ions is 7.88 \AA^3 , while the volume of one Ca-ion, which replaces two Na-ions, is only 4.99 \AA^3 . The "empty" space can thus be filled with water molecules. This mechanism leads to the conclusion that *permutits with divalent cations are more hydrated than permutits with monovalent cations*, provided the ingoing and outgoing ions are of somewhat similar size, such as, for example, Li and Mg, Na and Ca, K and Ba. From analogy with monovalent systems it would be expected that within the divalent lyotropic series, the hydration decreases from Mg-permutit to Ba-permutit, according to the size of the divalent ions.

3) *The H-system*: Extending the ideas so far developed to H-systems, the conclusion follows at once that these should contain the most water of hydration. The H-ion is the smallest ion of all, it occupies very little space in the cavity which, therefore, can be filled with H_2O molecules nearly to the maximum of its water holding capacity. For instance, if a Na-permutit is converted into a H-permutit, the "cavity-water" should be increased at about the rate of one water molecule per Na-ion replaced. Data indicate, however, that the number of water molecules in H-systems is considerably greater than that provided by mere space relationships. The author believes that the additional water molecules represent *water of constitution* formed during the process of replacement. Remembering that aluminum silicates consist of a framework of oxygen, and possibly hydroxyl ions, it can be easily imagined that replacement of cations by H-ions creates "potential water molecules" which are liberated upon ignition of the new compound. Fig. 21 illustrates schematically this formation of crystal lattice water molecules as a consequence of replacement of cations by H-ions.

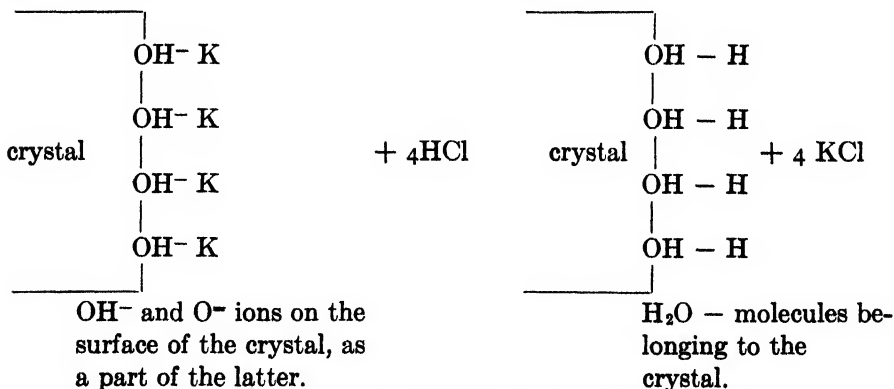


FIG. 21. Formation of crystal lattice water by adsorption of H^+ .

Before the exchange the analyses of the water-free colloidal particle would yield $x\text{SiO}_2$, $y\text{Al}_2\text{O}_3$ and $z\text{K}_2\text{O}$, while after exchange H_2O would be found in place of K_2O .

The hydration of the H-system is thus considered to consist of at least two main parts. First, the ordinary water of hydration (water films around the

colloidal particles and cavity water) and second, water of constitution. This water of constitution also explains why in many cases the H-systems exhibit a lower exchange capacity than the original zeolite complex, and furthermore it may account in part for the well known observation that ignition destroys the ionic exchange properties of the colloid.

Summarizing, it can be said that size consideration in ionic exchange can plausibly explain the observed relations between water adsorption of permutit *gels* and the nature of adsorbed ions (even including the abnormal H-system). For natural soil colloids (clay, bentonite-sols) complications may occur on account of differences in crystal structures and variations of size of colloidal particles due to ionic exchange and its consequent changes in the electrokinetic potential. In such systems the effect of the hydration of the ions in the outer surface and the polarization of water molecules due to the surface oxygen ions may overshadow to some extent the rôle played by the cavities.

General Summary

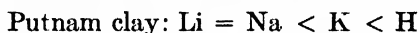
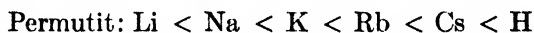
1) Ionic exchange (replacement of cations) has been studied in various artificial and natural aluminum silicates such as permutit, zeolite, Putnam clay and bentonite.

2) Electrodialyzed colloidal aluminum silicates contain exchangeable hydrogen ions and behave in many respects as colloidal acids. The strength of these acidoids varies as follows:



Permutit is the weakest acidoid.

3) In all exchange reactions very pronounced lyotropic series can be observed. The position of the various elements within the series varies according to the nature of the aluminum silicate. For the *adsorption* (intake) of monovalent cations the following relationships were found:



The *release* or outgo of adsorbed cations takes place in the reverse order of the intake.

4) The explanation of the individual behavior of the cations in the exchange process is based on Coulomb's law which expresses the magnitude of attraction existing between negative oxygen ions of the crystal lattice and adsorbed cations. Accepting the ideas of Wiegner, stress is laid on the radii of hydrated ions. It appears that these "hydrodynamic" radii vary according to the nature of the colloidal system.

5) The strong adsorption and difficult release of the hydrogen ion is easily understood by considering the strong chemical bonds existing between the adsorbed hydrogen ion and the oxygen and hydroxyl ions of the rigid crystal frame.

6) Ionic exchange affects the hydration of the colloidal particle. On the basis of space relationships it is suggested that clays with adsorbed divalent

cations should contain more water than clays having monovalent cations. H-systems are necessarily most hydrated.

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A STUDY OF THE STRUCTURE OF ELECTRODEPOSITED METALS.

PART II

BY L. B. HUNT

In an earlier paper¹ the writer has adumbrated a theory of the interference with crystal growth by ions, molecules or particles, other than those which constitute the metal being deposited, but no detailed suggestions were put forward of the precise mechanism by which this interference occurred. The present communication constitutes an attempt to elucidate this mechanism by means of a further and more detailed consideration of the processes occurring at the interface between cathode and electrolyte, in conjunction with the published data on the inclusion of foreign bodies within electrodeposits. In order to arrive at definite conclusions it has been necessary to start from the fundamental mechanisms of crystal growth and metallic cohesion, with particular reference to the concept of the two-dimensional lattice, and thence to develop a mechanical picture of the formation of this lattice from a more highly disperse phase during cathodic deposition. The ground having been cleared in this way, two further lines of thought have been developed. In the first place the problem has been treated as a case of surface chemistry. The interface cathode-electrolyte presents unusual and complicating features which render generalisation difficult. The constant renewal of surface which is occurring is particularly favourable to adsorption, but various bodies are present which may be adsorbed to a greater or less extent. Several workers have ascribed the influence of substances such as gelatin to adsorption, but have given no clear indication of the manner of this adsorption.

Secondly, the two-dimensional lattice idea has been further considered, and a new concept has been introduced of a two-dimensional lattice distortion, leading to changes of orientation and consequent refinement of grain. This concept has been applied to the data on the electro-deposition of alloys and of those metals with which hydrogen is co-deposited. Two distinct types of interference have thus been recognised, occurring respectively between, and during, the formation of the two dimensional lattices. It is fairly certain, however, that the transition from one to the other is not discontinuous in such cases as the discharge of complex cations and solvent sheaths, i.e., when the interfering particles are already attached to the metal ions. There is also the possibility, of course, of both types of interference occurring in any one case.

A number of investigators have referred to two other processes as influencing the structure of electrodeposited metals, viz. cataphoresis, and "mechanical inclusion" of the electrolyte or of colloidal particles. Now although cataphoresis may account for the arrival of particles at the cathode, some such process as adsorption must be brought into play to cause their ultimate cohesion to the cathode, whilst mechanical inclusion is of doubtful

existence, and in any case has no fundamental bearing on the problem in hand. These two processes have therefore been omitted from consideration at the present time.

The Mechanism of Lattice Formation

Current ideas on the subject of crystal growth are definitely in favour of a discontinuous process occurring by layers. It is a simpler matter to visualise the formation of a two-dimensional lattice in the process of crystallisation from the molten state, in which case the distribution in the two phases is substantially the same. Any attempt to form a mechanical picture of this lattice formation during cathodic deposition, however, introduces several complications, chief among which is the very great difference in distribution of the metal ions in the two phases. Other factors tending to obscure the picture are the deposition of only one kind of ion, in contradistinction to the building up of crystals of inorganic salts, and the nature of the electrical forces involved which on a priori grounds makes any suggestion of a pause in the process of deposition difficult to uphold. More so than with any other process of crystal growth, it is obviously impossible for deposition to be a continuous process, or for a two-dimensional lattice to be laid down in its entirety. The only alternative is therefore a gradual laying down of the lattice in such a way as to satisfy the conditions of distribution and the supply of free electrons. Carrying the process of elimination a stage further, general considerations and experimental observations on crystal growth suggest the extreme unlikelihood of a random deposition of ions at more or less isolated points until a layer is complete. In those cases of deposition referred to in Part I as "cathodic reproduction" very extensive and uniform layers have clearly been formed in order to continue the orientation of the underlying crystals without imperfection.

Volmer² postulates an adsorption layer of ions in a state intermediate between that of the electrolyte and that which they will take up in the lattice, but bases his ideas of the subsequent lattice formation on the assumption of the surface mobility of the adsorbed ions. This concept is obtained by analogy with the growth of mercury crystals by deposition from the vapour phase. This process, however, involves uncharged atoms only, and it is quite likely that in this condition the mercury atoms arriving at the surface of the growing crystal may cohere primarily with van der Waals' forces and may possess lateral mobility. In the case of electrodeposition, on the other hand, positively charged ions are approaching a negatively charged surface, and the writer cannot agree that surface mobility in these conditions of powerful binding is possible. Volmer found by oscillographic measurements (during which the amount of current passing was so small that concentration polarisation was absent), that the polarisation accompanying the deposition of zinc on large well-formed zinc crystals was quite appreciable, whereas with zinc amalgam and finely crystalline zinc foil as cathodes, no perceptible polarisation was recorded. This result he ascribed to a retardation on the part of the metal ions entering the solid lattice, caused by fluctuations in

thickness of the adsorbed layer, whilst in the case of the fluid electrodes, discharge and entry into the fluid phase constitute a single process. In the case of the finely crystalline electrodes the actual surface area may have been considerably greater than the apparent area.

The existence of an adsorption layer of metal ions on the surface of a cathode is a reasonably justifiable assumption in view of the work of Langmuir and others, coupled with the much older concept of a double layer due to Helmholtz and Lippmann. By making this assumption, however, the problem of the manner in which the layer is formed and maintained is still left unsolved. Presumably metal ions in the vicinity of the cathode will frequently be in collision with the cathode surface, and will tend to adhere thereto, prior to the passage of a current, although this will apply in greater or less degree to all ionic and molecular species present. On passing a current, however, the anions will be repelled violently, leaving an adsorbed layer of cations from which deposition can take place provided the potential requirements are satisfied. As deposition removes the metal ions the layer must be replenished by the process of diffusion. The process of deposition can therefore be roughly represented thus:

Diffusion \longrightarrow Adsorption \longrightarrow Lattice formation.

The final velocity will naturally be governed by the slowest stage in the process. The speed of diffusion will be determined by the concentration gradient across the diffusion layer, as also will the speed of adsorption. Increase of temperature, agitation of the solution and decrease of current density will thus promote diffusion, and adsorption from the diffusion layer. The concentration gradient, however, will depend upon the amount of deposition occurring, and thus on the current flowing. The delivery of electrons at the cathode surface is thus the determining factor, but certain complexities are introduced when the mechanism of this process is considered.

The Electron Theory of Metals and Metallic Cohesion

The majority of workers in this field have dealt mainly with the mathematical aspect of the problem, and it has become more and more apparent, as the wave nature of electrons has been established, that the formation of a mechanical picture should not be attempted. Certain general conclusions may, however, be drawn as to the inner structure of a metal as it affects the building up of a lattice at the cathode. This process consists fundamentally of the passage of the conduction electrons through the cathode until on reaching the surface they are captured by the metal ions, arriving from the opposite direction. There are therefore two points on which information is desired; firstly, as to the manner in which the electrons arrive at the cathode surface, and then as to the manner in which they cause the cohesion of the newly formed two-dimensional lattice to the bulk of the cathode.

In the first place, it is known that comparatively few of the electrons present in a metal are concerned in the conduction process, which comprises a relatively slow drift superimposed on the very rapid random movement of

the electrons. The concepts of the manner in which the electrons exist in a metal vary from the interpenetrating lattice theory of Lindemann,³ supplemented by Sir J. J. Thomson⁴ to involve the movement of chains of electrons along the lattice, to the free electron-gas theory of Sommerfeld,⁵ whilst Barlow⁶ has suggested a resemblance to an incompressible fluid rather than to a gas. Bloch⁷ has adopted the view that, whilst the conducting electrons are free, their motion is not completely haphazard, as postulated by Sommerfeld, but is a motion in a periodic field of force of which the period is the same as that of the atomic lattice. The electrons may then be regarded as both free and bound, i.e., as jumping from atom to atom and pausing for a time at each. Lennard-Jones and Wood⁸ have further discussed the electronic distribution in metals and have obtained a partial solution which is particularly interesting from the present point of view. A complete solution for a three-dimensional metal was not attempted, but the problem was simplified to that of a hypothetical two-dimensional lattice. For further details and the resulting diagram the original paper must be consulted, but the authors concluded that regions of greater electron density exist between the nuclei, and that the electrons within these regions are to be regarded as shared between the four surrounding nuclei (still retaining the two-dimensional concept), since they cannot be definitely associated with any one nucleus. These shared electrons apparently constitute a lattice array interpenetrating that of the nuclei, similar to the suggestions of Lindemann and Sir J. J. Thomson, but differing in that the system is not static even at the absolute zero. Those electrons which have sufficient energy will cross the equipotential lines and be able to travel from end to end of the metal, causing a continual interchange of electrons.

This, however, does not advance the solution of the problem of how the slow drift of the conduction electrons accounts for the cohesion of a metal ion *on every lattice point*. Barlow, however, observes that the pressure of the applied E.M.F. will be sufficient to cause only a limited number of gaps to be bridged by the conducting electrons, so that their flow will be restricted to paths that are continually changing. The electrons will always be attempting to move forward, but they must wait until an opportunity offers. It seems to the present writer that the most probable mechanism of the arrival of electrons at the surface, in the case of electrodeposition at all events, is in a succession of waves at right angles to the direction of flow, which will appear as somewhat analogous to a creeping barrage passing continually over the face of the cathode. It has already been said that the formation of a mental picture of this type is in many cases unjustifiable, but there are definite objections to being too easily dissuaded from the particle concept in the present case, such as the relations expressed in Faraday's laws, and the orderly arrangement of the lattices resulting from the interaction of metal ions and electrons, despite the indeterminate nature of the conduction process. If an imaginary plane is taken through the cathode, normal to the direction of flow of the current, and similar to Lennard-Jones' two-dimensional lattice, it is clear that all the conduction electrons cannot be moving simultaneously.

There must, therefore, be either a random here and there movement (an idea which is immediately discounted), or a wave-like oscillation, having an amplitude of the same order as the mean free path of the electrons themselves, and a frequency dependent upon the applied E.M.F. The passage of this wave train through the adsorption layer will naturally govern the formation of the next adsorption layer, and the whole process will thus be governed by these electron waves.

As regards the nature of metallic cohesion, Hume-Rothery⁹ suggests that the reason underlying the formation of this particular type of bond is that there are insufficient valency electrons for each atom to complete its octet by sharing one electron with each of several neighboring atoms. An atom of Group N will normally tend to complete its octet by sharing one electron with each of $(8-N)$ other atoms. When, however, there are less than four available valency electrons, each atom can no longer share one electron with more than four other atoms. When this occurs a bond must be formed in which an electron can be associated with more than two atoms. This bond will thus resemble the normal covalent bond in which an electron is shared between two atoms, but differ in that a larger number of atoms will share a valency electron. The point then arises of the difference between the cohesive forces in adsorption and in lattice formation, i.e., the difference between an adsorbed ion and a "discharged atom." The obvious conclusion is that the difference is due to the presence of the excess valency electrons. If the supply of electrons were cut off, adsorption would also cease, since the adsorption layer would no longer be incorporated into the metal lattice, thus forming a new surface on which further adsorption can take place. It is probable, therefore, that the adsorption of metal ions comprises an electrostatic type of adhesion in which the adsorbed ions attach themselves by the mirror image forces to the surface, without interfering with the cohesion bonds in the lattice. The supply of electrons by conduction will then operate to incorporate the adsorbed layer by the covalent electron-sharing linkage. Reverting to the wave concept of electrons, the transition from ion to "atom" may then be considered not as a sharply defined process, but as a merging of one into the other.

Interfacial Phenomena

The existence of an adsorption layer at the interface cathode-electrolyte has been the basis of the foregoing discussion, and it now becomes necessary to examine in more detail the conditions in this layer with respect to the various ionic and molecular species present in the solution. The constant renewal of surface which occurs cannot but be favourable to pronounced adsorption effects, and in these circumstances the experimental fact that adsorption of species other than the metal ion takes place to a very limited extent requires a word of explanation. The point of immediate interest is to consider the forces operating on a metal ion approaching a cathode. Firstly, there is the force due to the electrical field, which is responsible for the migration of the ions, and extends throughout the electrolyte. Secondly, there is the short

range electrostatic force between the cathode and the ion, and also the van der Waals' cohesive forces. In the opposite direction there are the retardations due to the anionic atmosphere and the solvent sheath respectively.

Now the ionic atmosphere, according to the Debye-Hückel theory, is continually building up in front, and dying away in rear, of a moving ion. When a cation reaches a point a few angstroms away from the cathode, therefore, the building up must cease and the dying away become more complete, owing to the repulsive forces on the anions prohibiting their close approach to the cathode surface. The resultant force on a metal ion passing through this

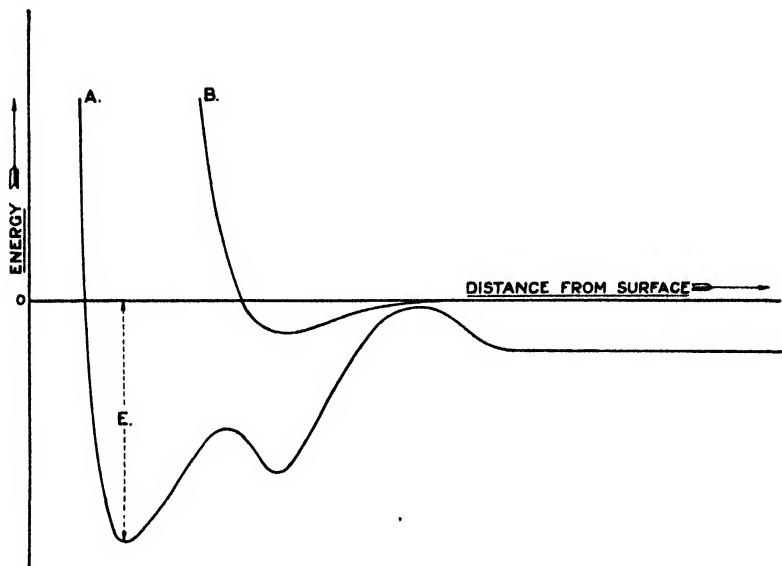


FIG. 1

Variation in potential energy with distance from cathode surface

part of its course will thus be first a slight retardation, followed by an increased attraction. The next event will be the repulsion of the solvent envelope, which will cause a further increase in potential energy of the ion, again followed by a sharp fall, to the point where the ion is held by the electrostatic forces, vibrating about the position of minimum potential energy, pending the arrival of one or more electrons to bring about ultimate cohesion. The potential energy of a metal ion as a function of its distance from the cathode surface is represented diagrammatically in Fig. 1 by curve A.

This curve is at best a first approximation, largely owing to the complexities introduced by the superposition of an electrical field on the more or less normal adsorption phenomena, but it is now tentatively put forward as a basis for future discussion.

Discharge of the ion will occur only if the neutralisation potential E , of Gurney,¹⁰ be greater than the work function of the metal ϕ , less the applied potential difference V . This neutralisation potential is defined by

$$E = I - W$$

where I is the ionisation potential of the ion, and W represents the energy of solvation, which must be replaced on discharge. The condition for discharge is then given by

$$E = I - W > \phi - V$$

Various other cations are usually present in the electrolytes employed for deposition, but except in cases of alloy formation, which will be dealt with later in the paper, they are never found in the deposit. The inference is that ions such as those of the alkali metals are not only incapable of being discharged, but on colliding with the cathode, have less tendency to be adsorbed, and are more likely to be reflected into the solution, in accordance with their relative ionisation potentials. This will result, however, in a building up of the concentration of alkali metal salts in the vicinity of the cathode, with a consequent decrease in the dissociation of the metal ions.

The adsorption of molecules will not be affected by the electrical field, but the ions of the metal lattice will cause the formation of induced dipoles in the molecules, which together with the long range van der Waals' forces will bring about adsorption. The potential energy of a molecule or solvent dipole is represented in Fig. 1 by curve B. There will be a small minimum at a greater distance from the surface than was the case with a metal ion, from which it is clear that molecules may be adsorbed in a layer above the ionic layer. They will, however, be comparatively loosely bound, and will thus possess an appreciable chance of escaping back into solution. They will also possess a certain amount of lateral mobility, according to Volmer's observations,² and it may be necessary for stable nuclei or groups to be formed in this way before adsorption becomes possible.

Solvent sheaths present a transitional case, in that the molecules are already bound to the metal ions, and that they arrive in more or less stable groups. However, the chance of their survival as far as the adsorption layer is considerably reduced by the increased concentration of metal ions in the two dimensional state. The possibility of their inclusion is nevertheless not to be ignored, as was indicated in Part I of this paper.¹ The above explanation merely accounts for the infrequency of the process. In this connection some results obtained by Aten, Hertog and Westenberg,¹¹ in the absence of solvation are instructive. Experiments were carried out with fused electrolytes and it was found that although the grain-size of electrodeposited silver, copper and nickel, was still dependent upon temperature and composition of bath, the wide differences which exist between the structures of these metals when deposited from solution disappeared. In general the grain-size was much larger than in deposits from solution. Van Liempt¹² has also obtained coarse-grained deposits of tungsten from fused electrolytes.

A similar transitional case is presented by the deposition of complex cations, such as Fuseya¹³ and his co-workers have investigated in copper sulphate electrolytes. Here again the molecular species arrive at the cathode already bound to the metal ion, but their concentration will not be reduced to the same extent as will that of the solvent molecules. The probability of their

becoming adsorbed and included is thus much greater. Fuseya ascribed his results to "discharge" of the complex ions, but his curves bear every resemblance to adsorption isothermals. Fuseya,¹⁴ however, could not obtain the same results with lead and zinc electrolytes, although complex ion formation was found. This failure he ascribed to the decomposition of the complex ions in the film of more alkaline solution near the cathode.

The Inclusion of Basic Matter

A more interesting phenomenon which has recently received attention concerns colloidal hydroxides or basic salts precipitated in the cathode film owing to the decrease in hydrogen ion concentration caused by the discharge

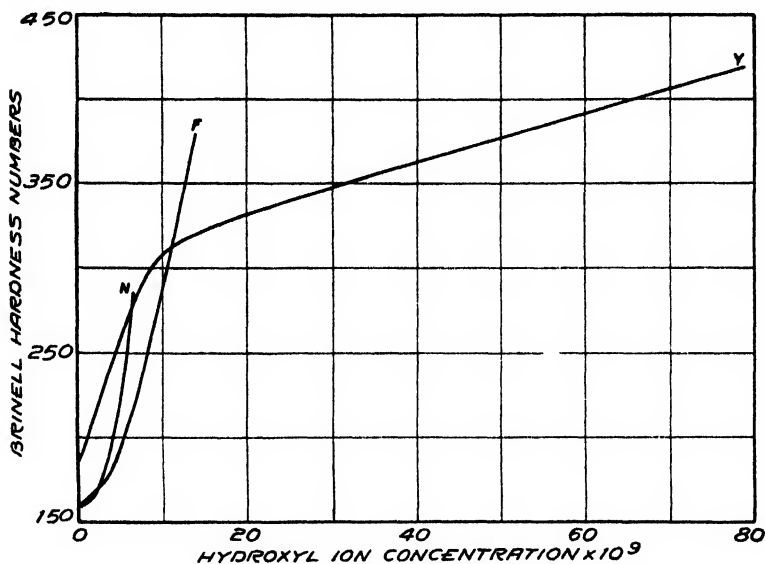


FIG. 2

of hydrogen. This was first investigated by O'Sullivan,¹⁵ who concluded that in the case of nickel sulphate electrolytes the hydroxide entered the deposit and influenced its structure. Macnaughtan and Hammond¹⁶ have recently extended this line of work, using Brinell hardness as a criterion of grain size in the deposit. It was found that the acidity of the electrolyte exerted a marked influence upon the hardness and structure of the deposit. In general a low acidity favoured the formation of hard deposits having a finely crystalline structure, whilst greater acidity favoured the formation of softer deposits having a larger grain size. Further, it was found that the hardness did not increase uniformly with increasing pH, but rose suddenly after a certain critical pH value had been reached. The present writer,¹⁷ however, has drawn attention to the somewhat illogical method used to represent the results of these workers, namely, the plotting of Brinell hardness against pH. By recalculating to hydroxyl ion concentration and plotting the results obtained

against Brinell hardness the writer has obtained curves of a different type, shown in Fig. 2 which bring out more clearly the differences between the electrolytes containing ammonium ions and those free from ammonia, owing to the different types of buffer action exerted. It appeared that whereas with the electrolytes N and F containing boric acid and sodium fluoride the amount of inclusion increased rapidly with increasing hydroxyl ion concentration, in the solution γ , containing ammonium sulphate the rate of increase of hardness fell away as hydroxyl ion concentration increased. While the latter effect might well be due, as suggested by the authors, to the tendency of the precipitated matter to redissolve in the ammoniacal solution in the vicinity of the cathode, the mechanism of the inclusion remains unexplained.

Adsorption in the true sense of the term is clearly insufficient to account for the increase in the amount of inclusion with increasing hydroxyl ion concentration, which fact of itself suggests a more direct mechanism of inclusion. The writer would therefore suggest that this mechanism consists of the discharge of a complex ion containing the metal hydroxide, or of an ion to which the colloidal basic matter is attached. In this connection it is interesting to note that Brdicka¹⁸ has recently investigated the hydrolysis of cobaltous chloride solutions at the dropping mercury cathode, and has concluded that deposition may occur from the ion $[\text{Co}(\text{H}_2\text{O})_6 \text{OH}]^+$.

The deposition of basic matter is also a factor of importance in the electrodeposition of chromium.

Sargent¹⁹ stated that the first stage in the process of electrolysis of chromic acid was the formation of a film of basic chromium chromate on the cathode. This was followed by a partial reduction of chromic ions to chromous ions, and deposition from both types with simultaneous evolution of hydrogen. Liebreich²⁰ suggested that metallic chromium was obtained by secondary reduction of the divalent hydroxide $\text{Cr}(\text{OH})_2$, in the cathode film, basing his statement on the fact that the metal is found beneath a layer of hydroxide when deposited from almost neutral electrolytes. The smaller the OH' concentration the greater would be the tendency for chromium to be deposited free from hydroxide. Müller²¹ agreed that the film at the cathode was composed of chromic oxide or chromic chromate, but maintained that deposition took place from the hexavalent ion. The sulphate radical was supposed to destroy the film and allow chromic acid to reach the cathode and be reduced, whilst in the absence of the sulphate or other radical the diaphragm (then invisible) was assumed to be "ideal." Small ions such as the hydrogen ion would be able to pass through the diaphragm, but large anions would be unable to follow. This concept has been criticised by Ollard,²² who showed that electrophoresis, which was held by Müller to be responsible for pressing the diaphragm against the cathode, was unfavourable in the chromic acid solutions employed.

As regards the actual inclusion of basic matter in the deposit, Adcock²³ found that chromium contained considerable amounts of oxygen in a form from which insoluble Cr_2O_3 was produced by heating in vacuo. The original oxygenic matter dissolved in dilute acid without residue, suggesting that it was not Cr_2O_3 , and no evidence of the presence of the electrolyte could be

found on crushing the deposit. The inference is that basic matter was included in the deposit in a manner analogous to the inclusions found by O'Sullivan and by Macnaughtan and Hammond.

Britton and Westcott²⁴ have also recorded the deposition of basic matter from solutions of chromic sulphate and chromic chloride. Furthermore these workers²⁵ have recently found as much as 13% of hydroxide matter included in the apparently metallic portions of the deposit. The writer considers that the concept introduced above to explain the inclusion of basic matter in nickel deposits will also suffice to account for the presence of such inclusions in chromium deposits, and also for the observed diaphragm formation. The colloidal particles are considered to be attached to the metal ions in the adsorption layer, and whilst this layer is static it will naturally not be visible. When deposition occurs, however, with the accompanying evolution of hydrogen, large amounts of basic matter will be brought up to the cathode. Small amounts will certainly remain adsorbed, and so become included in the deposit, but the major portion will be separated from the metal ions. The adsorbed layer will then thicken and become detached from the surface, thus becoming visible as a diaphragm in contradistinction to the breakdown of a molecular film, which merely results in molecular dispersion or solution. This concept appears to agree well with the results of Förster and Deckert²⁶ who, working with stannous sulphate electrolytes to which *m*-cresolsulphonic acid had been added, found that whilst the effect of adsorbed molecules was prolonged, the colloidal matter was rapidly exhausted, the effect increasing with increasing current density. In the case of basic matter, of course, the supply of colloidal particles is continuous owing to the constant evolution of hydrogen causing a rise in pH of the cathode layer. The process will differ considerably from the normal phenomenon of adsorption in that the amount of inclusion will increase regularly with increasing concentration of basic matter in the cathode film. The number of metal ions having colloidal or basic matter attached will necessarily be only a small fraction of the total number of metal ions proceeding to the cathode, this fraction being dependent on the hydroxyl ion concentration.

The Deposition of Foreign Cations

In certain cases of electrodeposition there are two principal cations entering the deposit. One of these may be the hydrogen ion, as is the case with the metals of the transitional group, or both may be metal ions, leading to the formation of an alloy. Now deposits formed in this way from two ions are well known to possess finely crystalline structures. For instance, nickel, cobalt or iron, deposited from solutions of their simple salts, are invariably of much finer structure than metals such as copper and zinc deposited under similar conditions. Further, deposits of two metals which normally yield coarsely crystalline deposits alone, are found to give fine-grained alloys. In the foregoing discussion foreign bodies which presumably enter, or rather cause, the grain boundaries of the deposited metal, have been the chief concern, but it is clear that foreign ions which enter the lattice have also to be

taken into consideration. In the case of alloy deposition the variable factors such as current density, temperature, agitation, etc., instead of influencing the structure of the deposit, merely serve to bring about alterations in its composition. No explanation of this finely crystalline structure has as yet been forthcoming.

The constitution of electrodeposited alloys has been investigated by a number of workers. Nakamura²⁷ found that the lattice constant of electrolytic brass containing 82% of copper showed no apparent difference from that of cast brass of the same composition. The deposit may therefore be presumed to consist of the normal α -solid solution of zinc in copper. Roux and Cournot²⁸ examined electrodeposits of copper-zinc, cadmium-silver, cadmium-zinc, and cadmium-nickel alloys, and found that the X-ray spectra could not be reproduced by superposition of those of the constituent metals, indicating that compounds or solid solutions, or both, were formed. Similarly Fuseya and Sasaki²⁹ examined their deposits of chromium-iron alloys and found them to consist of solid solutions. Stillwell³⁰ showed that in cadmium-silver alloys a number of phases consisting of both solid solutions and compounds were present.

Unfortunately the systems hydrogen-metal have received very little attention, and it is as yet quite impossible to state whether these systems represent solid solutions of the substitutional type, or solid solutions of the interstitial type (in which the solute ions are situated in the spaces between those of the solvent) or compounds. Yamada³¹ and McKeehan³² obtained the characteristic X-ray pattern for palladium, but found that the lattice was uniformly expanded by the presence of hydrogen. Linde and Borelius³³ concluded that both solid solution and compound formation occurred in the system palladium-hydrogen, whilst Hanawalt³⁴ considered that the compound Pd-H was formed. Evidence of the formation of a solid solution was obtained by Hüttig and Brodorb,³⁵ who found that the presence of hydrogen in electrolytic chromium caused a widening of the lattice without altering its form.

It is now established that the ions of a metal entering into solid solution replace those of the solvent metal in the lattice, so that the two kinds of ions are situated at random in a common lattice. If, however, the limit of solid solubility is exceeded a new phase must be formed in which the crystal structure differs from that of the pure metals, and which may consist partly of an intermetallic compound. The details of the concept of substitution in solid solutions have been worked out by Rosenhain³⁶ who in explaining the increased hardness of these phases suggested that solute atoms distort the lattice of the solvent metal, thus causing an increased resistance to slip. The writer proposes to adapt this hypothesis of lattice distortion to the case of a two-dimensional lattice in course of formation. In the solid three-dimensional state it is comparatively easy to visualise distortion producing hardness, but with a two-dimensional lattice the hardness factor is absent, and rigidity is greatly reduced. The writer suggests, therefore, that the presence of stranger ions in the two-dimensional lattice will cause distortion and breaking up of this

lattice with consequent changes in orientation and grain refinement. If the limit of solid solubility is exceeded a new phase must be formed, which will again be conducive to grain refinement. This type of interference with lattice formation clearly occurs in a plane parallel to the cathode, in contradistinction to the other types of interference which have been considered. The result of lattice distortion is therefore the production of a fibrous type of deposit, such as is invariably found with deposits of the transitional metals and of alloys.

Conclusion

The various types of interference with lattice formation which have been described are shown diagrammatically in Fig. 3, which represents the passage of the ionic and molecular species from the electrolyte to the cathode.

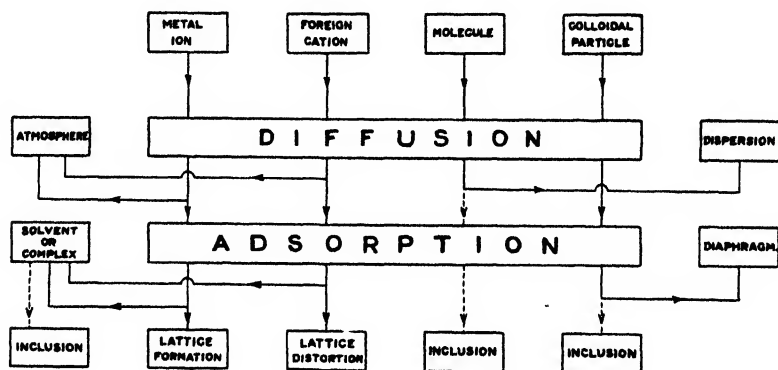


FIG. 3
The processes occurring at a cathode

Continuous lines indicate the major processes, and broken lines the processes of infrequent occurrence. The branching lines indicate the removal of certain types of ions and molecules from the cathode layer. Thus the first event on the approach of a cation to the cathode will be the loss of its anionic atmosphere, which will be followed by the loss of the solvent sheath or the complex portion of the ion. The latter may, as shown, remain adsorbed to a slight extent and thus be included in the deposit. The difference between the removal of molecules and colloidal particles is also indicated. Molecules adsorbed from the cathode will return into solution, whereas colloidal matter will not, and may accumulate temporarily as a diaphragm a short distance from the cathode, prior to its redistribution by diffusion or electrophoresis. Further, certain colloidal particles, more particularly those consisting of basic matter, will be adsorbed more firmly and in greater amount owing to their attachment to the metal ion, and will behave in a similar manner to complex ions.

The theory of interference with crystal growth proposed by the writer¹ receives considerable support from the lines of thought which have been developed in this paper. It is clear that no simple hypothesis, such as that

based on changes in polarisation, can be expected to account for the variations in structure of electrodeposited metals. Each species present in the electrolyte must be considered on its own merits with respect to the forces acting upon it, and its behaviour under these forces. It is considered that the adoption of this method has resulted in a more detailed insight into the mechanism of interference with crystal growth, and although the writer hopes to be able to present experimental data and more exact information bearing on the relative potency of the interfering bodies, it is his opinion that the first essential is an attempt to present a clear and logical account of the subject. By applying existing knowledge in the co-ordination of the available data and the further development of the hypothesis it is hoped that this object has been achieved.

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STATIC SORPTION ISOTHERMALS. ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

BY L. J. BURRAGE

1. Introduction

As the result of previous work on the discontinuous nature of sorption isothermals,¹ in themselves largely the outcome of a new method for the determination of sorption isothermals,² it was decided to carry out a further series of experiments using the static technique. This has the obvious advantage that the discontinuity cannot in any measure be due to the method employed.

The criticism which has been levelled at all previous work is that in no cases have points been taken closely enough together, in many instances a dozen points or so being deemed sufficient to cover the complete range of the isothermal. In the present work it was decided to start from a pressure of about 80 mm. and obtain points as close together as was possible, the main object in view being to determine, if possible, the exact number and position of the breaks.

2. Experimental

The technique employed was similar to that described in a previous paper.³ This was adopted after careful consideration of the only other method which was suitable for this type of work—the McBain Sorption Balance. It is not considered that the latter has any advantages over the method employed in the present work. In the sorption balance the quartz spring has first to be calibrated. This is achieved by noting the elongation of the spring on the addition of known weights to the cup, which is attached to the spring. When set up for use, charcoal is placed in the cup and the apparatus evacuated. A certain charge of vapour is admitted to the system, which is then allowed to come to equilibrium. One notes the position of the spring with a cathetometer to give the weight of substance adsorbed and reads off the vapour pressure on some type of manometer. This latter involves two readings on the cathetometer, if some type of U-tube manometer is employed.

In the method employed in the present work, it was necessary to know the volume of the apparatus accurately and then for each point on the isothermal four cathetometer readings were necessary, two for the initial pressure and two for the final pressure. It would appear that the accuracy of the latter method was not in any way inferior to that of the sorption balance, judging by the degree of reversibility which has been obtained.

¹ Allmand and Burrage: *Proc. Roy. Soc.*, **130A** (1931); *J. Phys. Chem.*, **35**, 1692 (1931).

² Burrage: *J. Phys. Chem.*, **34**, 2202 (1930).

³ *Proc. Roy. Soc.*, loc. cit.

Several refinements have been instituted in the method described in a previous paper, and it would be of advantage to describe the method in detail. The complete train (Fig. 1) consists of a Leybold mercury condensation pump backed by a Hyvac Oil Pump, a McLeod Gauge, a small section of narrow tubing about $2\frac{1}{2}$ inches long with taps at either end (A and B, the volume between these points being approximately 1.5 ccs.), and a freezer C, followed by a mercury manometer E. This is fitted with a tap in the 'closed' limb which

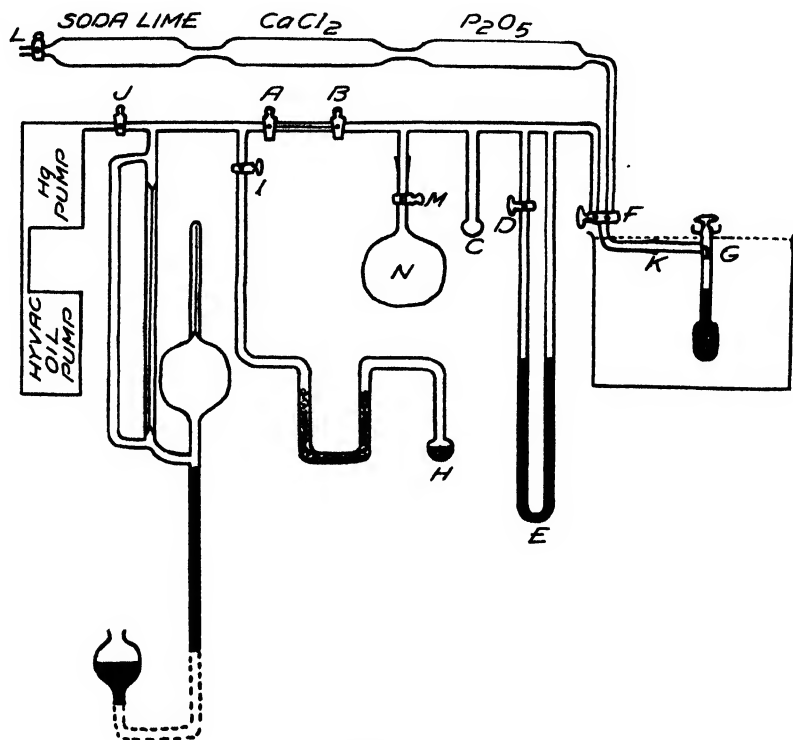


FIG. 1

is connected to the vacuum line, so that, if necessary, the manometer may be pumped out on the closed side. This is useful in freeing the mercury from the last traces of air, when the apparatus is first set up.

F is a two-way tap, one limb being connected to the vacuum line and one to the air. Attached to this latter limb are a phosphorus pentoxide tube, calcium chloride tube, and a soda lime tube. The container for the charcoal was attached to the common limb of this tap. This container G, made in silica, was exactly similar to that described by Chaplin.¹ Between the mercury pump and the tap A, a T-piece was inserted leading to a bulb which was shut off from the apparatus by a tap. This constituted the supply bulb.

It has been suggested that interference with the position of the breaks might be caused by the CO_2 on the surface which is constantly being driven

¹ Proc. Roy. Soc., 121A, 344 (1928).

off during the course of the experiment to a greater or lesser degree. Since the chief object in view in this investigation was the establishment of the exact pressures at which breaks occur, and also the quantity increment per break, when these are unaffected by disturbing conditions, it appeared that carbon dioxide might be a suitable substance to employ.

Since the carbon complex, C_xO_y , which covers the surface of the charcoal, exerts a pressure of carbon dioxide at ordinary temperatures, it seemed as though there was a probability that an isothermal with carbon dioxide might be somewhat less disturbed by those complications which have been present heretofore.

It was decided to work with a charcoal which was known to have a large capacity for carbon dioxide¹ and, D 1, a steam-activated coconut charcoal, (packing density = 0.575) was selected. About 2 gms. of this was sieved (10-12 mesh) and heated in an air oven at 150° to remove most of the adsorbed water to facilitate the evacuation. This is an important point in the evacuation of charcoals, which has been previously overlooked, as it lowers the time necessary for evacuation down to 10^{-4} mm. by at least 75%. This half-dried charcoal was packed into the silica container and attached to the evacuation apparatus, and pumped down to 10^{-4} mm. at room temperature. The temperature was then raised to 110°C. and the charcoal evacuated to the same pressure as before. The container was detached, cleaned with alcohol and ether, and weighed, and finally attached to the apparatus proper, the joint being made vacuum-tight with Everett's Wax.

The supply bulb on the apparatus was filled with sodium bicarbonate and the whole apparatus evacuated to a pressure of 10^{-4} mm., the tap on the container being kept shut during this operation. Between the supply bulb and the main apparatus a small U-tube, filled with phosphorus pentoxide, was inserted to free the carbon dioxide from water as it passed into the apparatus.

The taps J, leading to the pumping system, D, forming the closed limb of the manometer, and A, leading to the main apparatus were closed. Tap I was opened and the supply bulb H warmed until gas was evolved. A Dewar flask containing melting methylcyclohexane was put on the freezer C and the taps A and B opened to admit a charge into the apparatus, the two-way tap F being open, connecting with G. The freezing bath removes any traces of water which may have passed the phosphorus pentoxide. Tap B was now shut and the pressure read off on the manometer E. Then tap G was opened and when the pressure was constant the manometer was read again. Knowing the initial pressure, the final pressure after sorption, and the volume of the apparatus, the weight of carbon dioxide sorbed was found. This was repeated several times until sufficient carbon dioxide had been adsorbed to give a pressure of about 100 mm.

Tap G was then shut, and liquid air placed around the freezer C, the carbon dioxide between B and G being frozen out. The two-way tap F was then turned to admit air and the container removed for weighing. The air that is

¹ Allmand and Burrage: *Proc. Roy. Soc.*, **130A**, 610 (1931).

let into this portion of the apparatus is freed from water and carbon dioxide by passing over soda lime, calcium chloride and phosphorus pentoxide. Immediately the container has been removed, the open end of the tube K, where the container had been attached, was closed by a waxed glass stopper.

In this way the container can be removed at any time during the experiment without interfering with the pressure of carbon dioxide in the apparatus. The container was next reattached, the air being removed from the side arm system by means of a hand pump attached at L, the liquid air removed and the whole apparatus evacuated down to 10^{-4} mm. Taps A and B were closed and the container tap opened. When equilibrium had been obtained (which was almost instantaneous) the pressure was read off. Knowing the volume of the apparatus and the pressure, the weight of carbon dioxide lost by the charcoal can be calculated and hence the quantity corresponding to the new pressure.

The container tap was now shut and tap B opened and shut immediately, the time interval being approximately $\frac{1}{4}$ th second. By this means the pressure in the main apparatus was lowered to a very slight degree. The pressure was read off and the container tap opened, causing the pressure to rise slightly. The carbon dioxide lost by the charcoal was again calculated. Tap A was opened to the pumps and the carbon dioxide between A and B removed. Tap B was then shut and the apparatus was now ready for the next point. In this manner points may be obtained as closely as one may desire. When the pressure was low it was necessary to remove gas several times before a sufficient drop in pressure was obtained in the main apparatus.

If it was desired to remove the container during the course of the run to check the weight, the carbon dioxide in the apparatus between B and G was first frozen out in the manner which has been previously described.

The volume between B and G was determined by a sharing method and checked by a second process. A bulb N, provided with a tap, was joined to the apparatus by means of a ground glass joint M, sealed with Everett's wax. The volume of the bulb below the tap was accurately determined both by evacuation and filling with water—96 ccs. The bulb was filled with nitrogen at atmospheric pressure and attached to the main apparatus which was then evacuated. On opening M, a pressure developed in the apparatus. Knowing the initial and final pressures and the volume of the bulb, the volume of the main apparatus was calculated. The calibration was carried out with the container G in position. This determination was repeated several times, close agreement being obtained.

The volume was checked by filling G with charcoal and charging with vapour. In this way the loss in weight of the container gave rise to a certain pressure in a similar fashion to the first calibration. Good agreement was again obtained, the average value being 359 ccs. A correction was applied for the change in volume with change of level in the manometer tube but this was almost negligible, except at the higher pressures. The change in volume does not affect the pressure, since the latter is in equilibrium with the adsorbed carbon dioxide. It affects, however, the calculated quantity of carbon dioxide

adsorbed, which is in equilibrium with that pressure, but it was found that the error introduced in the calculated weight was exceedingly small.

The container was surrounded by a thermostat and the rest of the apparatus enclosed in a constant temperature box by which means an accurate temperature control was exercised. The dead-space volume of the container

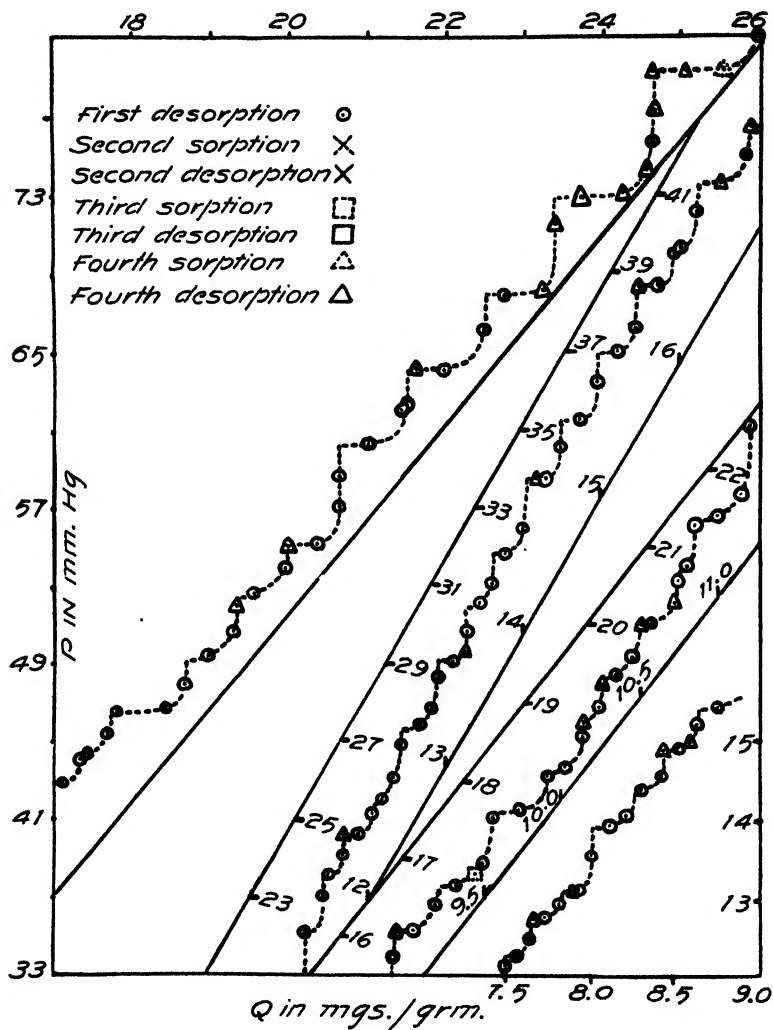


FIG. 2

was very small and could be neglected since the variation in the weight of carbon dioxide occupying this area was negligible in comparison with the weight adsorbed. In weighing the container a counterpoise of the same material and of approximately the same displacement and surface was used.

It should be mentioned that the frozen carbon dioxide, after its liberation from the bicarbonate was exhausted before measuring its pressure at 25°C . in

the apparatus, to remove any traces of permanent gas, this process being repeated several times. Tests for permanent gas were also made at intervals during the experiment but the results were always negative.

3. Results

Approximately 350 points have been obtained on the isothermal within the pressure range 81 mm. — 10^{-2} mm. at 25° . This comprises a desorption curve, a resorption, then a redesorption, followed by a second resorption and a further redesorption.

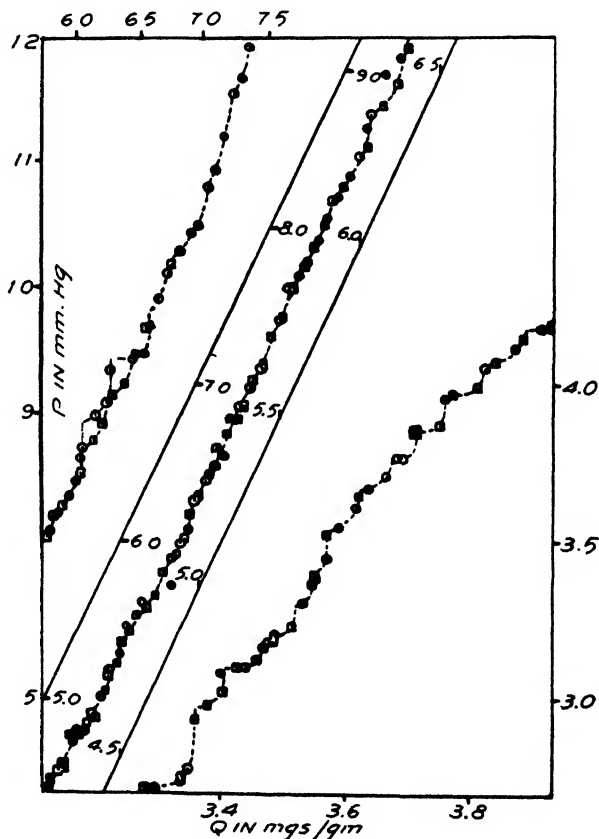


FIG. 3

Finally sorption was carried out to the initial pressure and then desorption to a considerable distance along the isothermal.

The pressure measurements were obtained with a cathetometer reading to 0.01 mm. and the pressure readings could always be reproduced to this figure. This was demonstrated by freezing out the carbon dioxide and then allowing it to vaporise and also by a redetermination of the meniscus after resetting the cathetometer.

For the sake of brevity all tables of figures have been omitted and the complete results are expressed graphically in Figs. 2-4.

One is justified in drawing the curves through each point and not taking a mean, since the experimental error of each point is very low, as is instanced by the reproducibility. If there were any serious error this reproducibility could not be obtained in an experiment employing this technique.

It should be noted, in passing, that the breaks are in no way due to drift as there was no change in the pressure 0.66—(Point 217) after the charcoal had

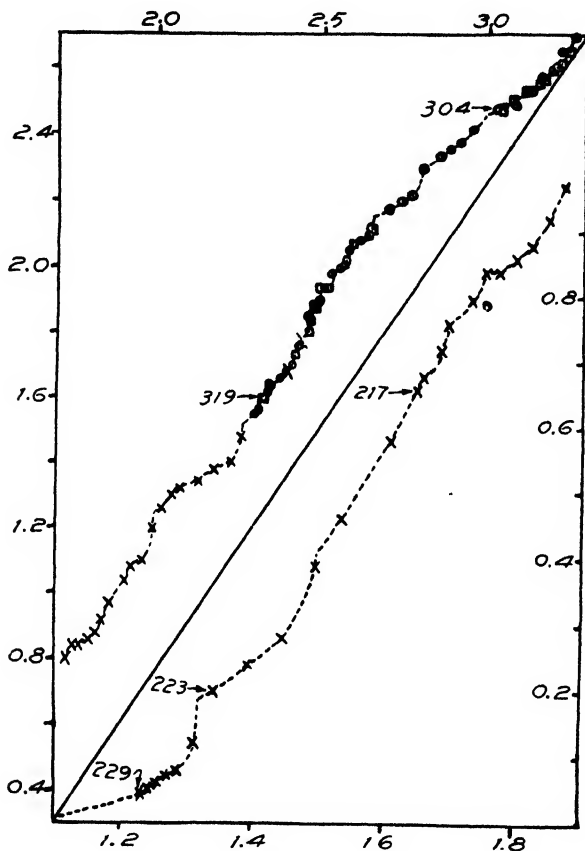


FIG. 4

been allowed to stand in contact with the vapour for 76 hours; similarly there was no change in the pressure 0.20 mm (Point 223) after 168 hours, while at 2.48 mm. (Point 304) on the next desorption series there was no change on standing for 5 months.

Once or twice during the course of the experiment the container was detached and weighed and the quantity so obtained compared against that obtained by the 'pressure change' method employed in this work.

At 0.04 mm.	Quantity = 1.23 mgs/gm (Pressure Change)
(Point 229)	= 1.5 mgs/gm (Weight)

At 1.6 mm. Quantity = 2.33 mgs/gm (Pressure Change)
(Point 319) = 2.6 mgs/gm (Weight)

It was not possible to compare the weights at the end of the experiment as, owing to an accident, air was allowed to enter the container.

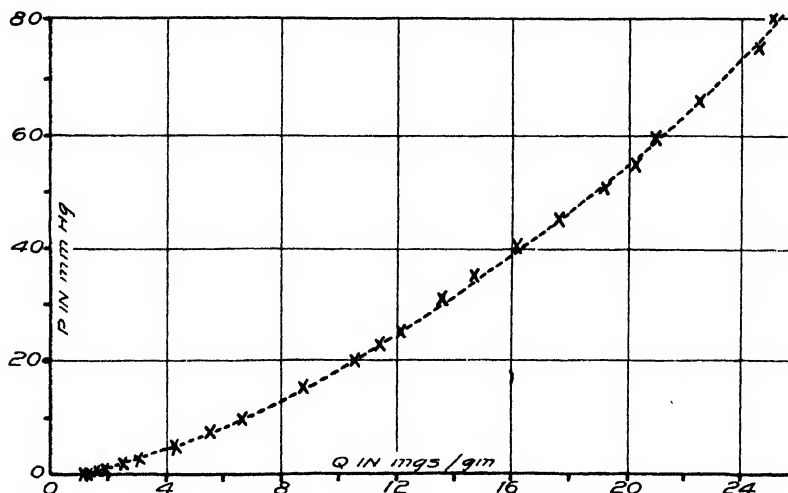


FIG. 5

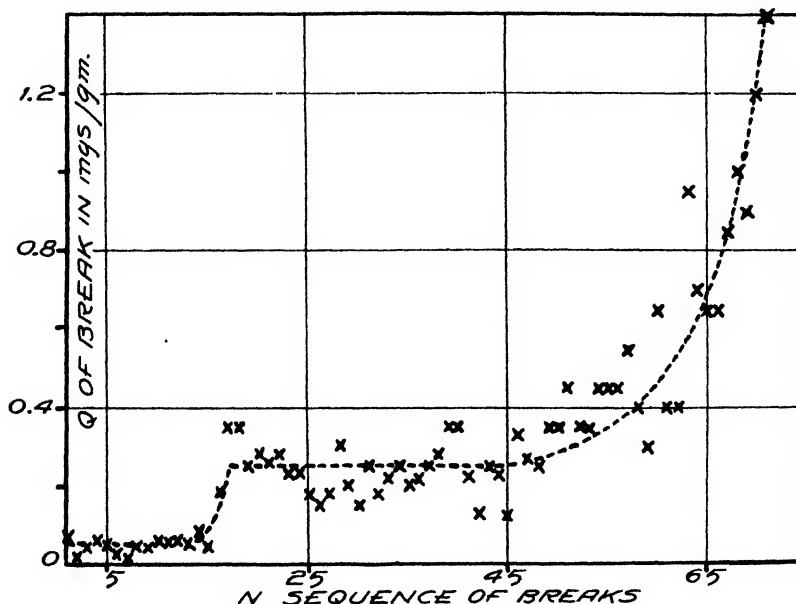


FIG. 6

The cause of the discrepancy between the weighed and calculated figures is not known and in any case is very small since a weight error of 0.5 mgm would account for the difference.

In Fig. 5 a selection of points from Figs. 2-4 have been plotted giving the course of the isothermal throughout the entire range investigated. As will be seen from the diagram a smooth curve has been drawn through the points, giving a normal type of isothermal. If this isothermal were plotted on the same scale, which is normally employed for vapours on charcoal (1 cm. = 1 mm. pressure or 10 mgs/gm quantity), a straight line could be drawn through practically all the points; this is in agreement with other results obtained in this laboratory.¹

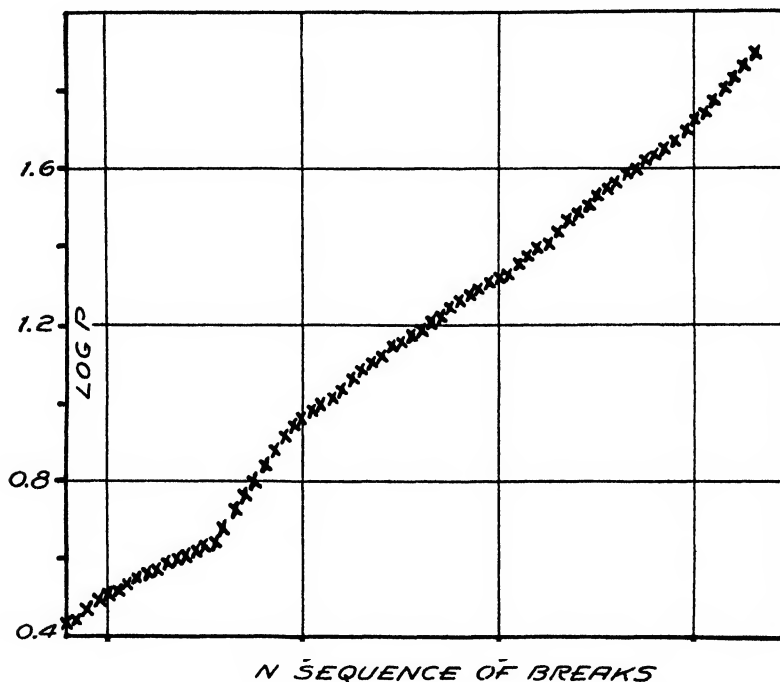


FIG. 7

Discussion

From Figs. 2-4, it will be seen that excellent reversibility has been obtained. The structure of the isothermal was found to be very complicated and a verification has been obtained of the discontinuities which have been found in other cases using different methods. The discontinuities previously noted, have only been observed up to a pressure of approximately 30 mm. In the present work this range has been practically trebled and still the breaks persist up to this pressure.

From this it would appear reasonable to predict that they would be found at whatsoever pressure the experiment was carried out, provided that the pressure exceeded 0.1 mm. and that the surface of the charcoal was not com-

¹ Allmand and Chaplin: Proc. Roy. Soc., 132A, 460 (1931).

pletely covered by the adsorbed molecules. In this connection it should be noted that in some high pressure adsorption measurements carried out by McBain and Britton¹ marked breaks were obtained. The authors, however, do not comment on this.

At higher pressures the breaks are almost rectangular, but this form tends to disappear somewhat at lower pressures when the pressure and quantity increments per break become very small.

In Figs. 6 and 7, respectively, the pressures at which the breaks occur, and the pressure increments for each break, have been plotted against the sequence of the breaks, commencing at a pressure of 2.72 mm., as the pressures and more especially the quantity values of the breaks are too small to allow of accurate definition below that point.

One interesting detail, which must be noted in passing, is that there is a very definite break at 0.06 mm., whereas in other cases there are no breaks below 0.1 mm. In a previous paper² mention is made of a break at 0.6 mm. in a water isothermal and this was considered to be due to carbon dioxide on the surface which had not been cleaned-up by the water vapour. Since carbon dioxide itself has a break in this region and vapours like carbon tetrachloride, which remove carbon dioxide with comparative ease, have not, providing that the surface has been sufficiently cleaned, this would appear to be a correct assumption.

Allmand and Puttick³ found a break in this region using carbon tetrachloride, but a desorption isothermal carried out after further resorption to a much higher pressure gave a break at approximately 0.1 mm., showing that the surface could not have been completely cleaned-up in the first case.

In Fig. 6, the log of the pressure of the break has been plotted against the sequence of the breaks, calling the first break plotted No. 1, etc. and in Fig. 7 the quantity increment per break has been plotted against the sequence of the breaks. Both of these plots show a marked tendency to regularity, especially that representing $\log P/n$. This was only to be expected since the pressure is probably less affected by foreign influences than is the quantity.

Assuming that each break marks the completion of a ring of molecules round all the activated points, then if foreign molecules are already present in the space where a given ring will form, the number of adsorbed molecules necessary to complete that ring will be fewer than would be expected and hence the quantity value for a given break is too small. There must, of necessity, be some effect on the pressure, but this will not be very marked unless a very large number of foreign molecules are present. Under these conditions, when the pressure reaches a value at which the ring should form, it is insufficient to anchor the molecules concerned and a greater force is needed, so as to expel the foreign molecules and thus allow the ring to be formed. Hence the pressure for a given break would be too high.

¹ J. Am. Chem. Soc., **52**, 2198 (1930).

² Allmand and Burrage: J. Phys. Chem., **35**, 1692 (1931).

³ Proc. Roy. Soc., **130A**, 197 (1930).

Although the diagram representing the curve in which q is plotted against N may not appear to be very regular, yet when it is noted that 1 cm. on the vertical scale = 0.1 mgs/gm, it will be seen that experimental errors will be greatly magnified.

In Fig. 3 the curve in the region of 9 mm. pressure is seen to be non-reversible over a range of approximately 0.7 mm. The second desorption cycle is to the right of the first pointing to a definite cleaning of the surface between the carrying out of these two cycles. Since the points coincide below this portion of the isothermal, it would appear to be due to a purely local disturbance. It cannot be ordinary experimental error as the figures would not have overlapped below this point.

It is not proposed to go into any theoretical discussion in detail as that will be reserved until further work, which is now in progress, has been completed. One thing, however, would appear to arise from this investigation, namely, that instead of carbon dioxide on charcoal giving rise to the simplest conditions, in point of fact it gives rise to the most complicated. It would appear that the carbon dioxide, which is adsorbed, changes over continuously into the complex C_xO_y , (a kind of surface compound) dependent on the pressure. As the pressure of carbon dioxide is increased more C_xO_y will form and *vice-versa*. This means that with increase of pressure the complex builds itself up outwards from the surface of the charcoal, forming a spongy mass, of which the molecules nearest the charcoal actually form the complex, with a continuous gradation to ordinary carbon dioxide molecules on the surface.

This hypothesis tends to shed light on the anomalous results previously obtained with carbon dioxide on charcoal¹ D_1 . It follows from the hypothesis that the amount of carbon dioxide adsorbed depends very largely on the degree of evacuation and this, in turn, depends on the ease with which carbon dioxide can diffuse away from the charcoal surface.

Again, from the hypothesis, it follows that the higher the initial charging pressure the more carbon dioxide may be more or less permanently transformed into the carbon complex. Since, in the previous work, the initial charging pressure at 25° was 4.58 mm. and at 40°, 8.04 mm., the statement that it would appear that less carbon dioxide was taken up at 25° than at 40°, could be easily explained.

The portion of the isothermal which will be principally affected by these conditions is the section which runs along the quantity axis, in other words, that quantity adsorbed, which is so firmly held, that it gives rise to practically zero pressure.

If this assumption be correct, it is obvious why such a complex curve should be obtained since one is dealing with two simultaneous effects. (1) The sorption of carbon dioxide and (2) the conversion of some of the previously adsorbed carbon dioxide to the complex C_xO_y . It is these two processes occurring together which probably prevents the rectangular steps being observed.

¹ Allmand and Burrage: Proc. Roy. Soc., loc. cit.

Summary

1. A careful study has been made of the carbon dioxide isothermal at 25° over a pressure range 81 mm. — 0.04 mm., some 350 points being determined.

2. The pressure and quantity increments of the breaks have been observed.

3. A hypothesis has been suggested for the complex nature of the isothermal.

The author wishes to express his thanks to Professor A. J. Allmand for the interest he has taken in this work.

*King's College,
London.
February 29, 1932.*

A MODIFICATION OF THE FREUNDLICH ADSORPTION ISOTHERM

BY WILLIAM ROGERS, JR. AND MARTIN SCLAR

Of the numerous theoretical and empirical adsorption equations which have been proposed,¹ that of Freundlich has been found to describe best the experimental facts, and hence has been used almost exclusively. The Freundlich isotherm may be used to calculate: (a) the mass of adsorbent necessary to cause a desired change in concentration or pressure, except where the equilibrium concentration or pressure is zero, and (b) the equilibrium concentration or pressure, when the initial concentration or pressure, the volume of solution or dead space, and the mass of adsorbent are known. But the latter calculation is very laborious even when carried out in the simplest manner.² The purpose of this paper is to modify Freundlich's equation so that it may be used for all the above purposes with the same efficiency, but with much greater ease. The modified equation also has the advantage that it may be used to calculate the mass of adsorbent just necessary for total adsorption.

Freundlich's isotherm for adsorption from solution is

$$x/m = k C_2^n$$

where x is the amount adsorbed, m is the mass of adsorbent, C_2 is the equilibrium concentration of the solute, and k and n are empirical constants.

For an infinitesimal adsorption the isotherm becomes

$$dx/dm = k C^n$$

But $dx = V dC$, where V is the volume of the solution, so that

$$VdC/dm = k C^n \quad \text{and} \quad VdC/C^n = k dm.$$

This equation may be integrated as follows:

$$V \int_{C_1}^{C_2} C^{-n} dC = k \int_m^0 dm$$

where C_1 is the initial concentration of the solution.

$$V/m (C_1^r - C_2^r) = k r$$

where $r = (1-n)$. Let $k r = K$ since both k and r are constants.

Then

$$V/m (C_1^r - C_2^r) = K \dots \dots \dots (1).$$

Solving equation (1) for C_2 :

$$(C_1^r - K m/V)^{1/r} = C_2 \dots \dots \dots (2).$$

When C_2 is taken as zero:

$$C_1^r V/m_0 = K \quad \text{and} \quad C_1^r V/K = m_0 \dots \dots \dots (3).$$

¹ Swan and Urquhart: J. Phys. Chem., 31, 251 (1927).

² Rogers and Sclar: J. Phys. Chem., 35, 2758 (1931).

Equation (1) is to be used to calculate the values of r and K if the method of trial and error is to be used. Equation (2) is used for a calculation of the equilibrium concentration when C_1 , m , and V are known. Equation (3) is used for a calculation of the mass of adsorbent, m_o , just required for total adsorption of the solute.

It is interesting to note that equation (3) is similar to one previously derived³ in a different manner. The latter equation, however, is restricted to constant volume.

The method used to derive equations (1), (2), and (3) may be used to derive a similar set of equations for the adsorption of gases.

The Freundlich isotherm for the adsorption of gases is

$$x/m = k P^n$$

where P_2 is the equilibrium pressure, and the other terms retain their previous meanings. If x is expressed in mols, then $x = n_1 - n_2$, where n_1 is the number of mols admitted to the adsorption chamber, and n_2 is the number of mols not adsorbed. Corresponding to n_1 and n_2 there would be an initial pressure P_1 and an equilibrium pressure P_2 respectively. The volume of the adsorption chamber less the volume of the adsorbent is V . Then assuming a perfect gas,

$$\begin{aligned} P_1 V &= n_1 RT & P_2 V &= n_2 RT \\ n_1 &= P_1 V / RT & n_2 &= P_2 V / RT \\ x &= V / RT (P_1 - P_2) & dx &= V / RT dP \end{aligned}$$

For an infinitesimal adsorption the Freundlich adsorption isotherm would become,

$$dx/dm = k P^n.$$

Substituting in this equation the value of dx from above,

$$V/RT \cdot dP/dm = k P^n \quad \text{and}$$

$$\int_{P_1}^{P_2} dP/P^n = kRT/V \int dm$$

Proceeding exactly as in the derivation of the equation for adsorption from solution, the results are:

$$\frac{V}{m RT} (P_1^r - P_2^r) = K \dots \dots \dots (4).$$

$$P_2 = (P_1^r - \frac{K RT}{V} m)^{1/r} \dots \dots \dots (5).$$

$$m_o = P_1^r \frac{V}{K RT} \dots \dots \dots (6).$$

Equations (4), (5), and (6) are to be used similarly to equations (1), (2), and (3) respectively.

Since $P_1 V = n_1 RT$

$$P_1/n_1 = RT/V$$

and these may be used interchangeably in any equation if to do so is more convenient.

¹ Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., 178.

The validity of equations (2), (3), and (5) will be seen in the following data. There are no data presented (because they are not available) in support of equation (6). But its validity may be assumed without much apprehension because of its similarity to equation (3), and its following directly from equation (5), both of which equations are supported by the data presented.

In the data listed, experimental and calculated values of equilibrium concentrations and pressures are compared. A brief examination of the data, especially that for adsorption of gases, will show that were the experimental and calculated values of x/m compared, as is the custom in demonstrating the validity of adsorption isotherms, the agreement would be better.

TABLE I⁴
Adsorption of Benzene in Ethyl Alcohol on Pure Carbon

C ₁ mol frac.	H/m millimols/g.	C ₂ obs. mol frac.	C ₂ calc. mol frac.
0.00653	372.2	0.00513	0.00504
.01286	333.6	.01050	.01057
.02604	356.5	.02289	.02298
.05273	366.8	.04854	.04861
.1090	354.7	.1033	.1031
$r = 0.54$		$1/r = 1.852$	$K = 3.20$

TABLE II⁴
Adsorption of Ethyl Carbonate in Ethyl Alcohol on Pure Carbon

C ₁ mol frac.	H/m millimols/g.	C ₂ obs. mol frac.	C ₂ calc. mol frac.
0.00339	525.0	0.00323	0.00324
.00696	455.2	.00667	.00667
.0142	399.9	.0136	.00137
.0293	514.2	.0286	.0286
.0610	404.3	.0596	.0594
$r = 0.28$		$1/r = 3.57$	$K = 1.37$

H in Tables I and II is the total number of millimols of both solute and solvent in the solution.

TABLE III⁵
Adsorption of Calcium Hydroxide on Basic Calcium Phosphate
 $m = 0.8614$ g. in each bottle

C ₁ g./l.	V cc.	C ₂ obs. g./l.	C ₂ calc. g./l.
1.176	224.69	1.099	1.089
0.6706	224.69	0.5910	0.599
.3335	224.69	.2805	.278
.1514	224.69	.1130	.110
.0907	224.69	.0579	.0572
.0470	224.69	.0207	.0216
.0205	221.69	.0029	.0034
$r = 0.65$		$1/r = 1.54$	$K = 14.1$

⁴ F. E. Bartell and C. K. Sloan: J. Am. Chem. Soc., 51, 1640-1641, Tables II and III (1929).

⁵ Lorah, Tartar, and Wood: J. Am. Chem. Soc., 51, 1103, Table II (1929).

TABLE IV⁵

Adsorption of Calcium Hydroxide by Tricalcium Phosphate
 $m = 0.3838$ g. in each bottle

C_1 g./l.	V cc.	C_2 obs. g./l.	C_2 calc. g./l.
0.4990	224.69	0.4525	0.4374
.2848	224.69	.2388	.233
.1390	212.69	.0989	.0961
.0699	224.69	.0348	.0379
.0278	224.69	.0043	.0059
.0188	224.69	.0011	.0010
.0110	224.69	.0002	.0000
$r = 0.7$	$1/r = 1.43$	$K = 31.5$	

TABLE V⁶

Adsorption of Sodium Hydroxide on Silica Gel
 $V = 1000$ cc. in each case

C_1 mol/l.	m g.	C_2 obs. mol/l.	C_2 calc. mol/l.
0.0127	43.8	0.0	0.0
.0264	42.8	.0016	.0015
.0371	43.5	.0036	.0036
.0667	43.6	.0118	.0130
.1325	43.5	.0447	.0427
$r = 0.4$	$1/r = 2.5$	$K = 3.73$	

TABLE VI⁷

Adsorption of Sulphuric Acid on Wool
 $V = 250$ cc. in each case
 $m = 1$ g. in each case

C_1 millimols/250 cc.	C_2 obs. millimols/250 cc.	C_2 calc. millimols/250 cc.
0.08	0.04	0.032
.16	.09	.088
.23	.13	.14
.38	.24	.26
.61	.43	.46
1.15	.91	.94
1.91	1.64	1.64
3.06	2.71	2.71
4.60	4.18	4.17
6.14	5.70	5.63
$r = 0.5$	$1/r = 2$	$K = 26$

⁵ Patrick and Barclay: J. Phys. Chem., **29**, 1401, Table I (1925).

⁷ Paddon: J. Phys. Chem., **33**, 1107, Table I (1929).

TABLE VII⁸
Total Adsorption of As by Fe(OH)₃
(with the addition of H₂SO₄)

V = 100 cc. in each case			T = 0°C		
C ₁ mg./100 cc.	m ₀ obs. mg.	m ₀ calc. mg.	C ₁ mg./100 cc.	m ₀ obs. mg.	m ₀ calc. mg.
0.1	1.6	1.97	200.	970.	1000.
5.0	56.	48.6	300.	1450.	1400.
30.	210.	211.	400.	1800.	1770.
60.	360.	373.	500.	2220.	2120.
100.	570.	567.	1.0	13.	13.
r = 0.82			K = 7.7		

TABLE VIII⁸
Total Adsorption of As by Fe(OH)₃
(without the addition of salt or acid)

V = 100 cc. in each case			T = 0°C		
C ₁ mg./100 cc.	m ₀ obs. mg.	m ₀ calc. mg.	C ₁ mg./100 cc.	m ₀ obs. mg.	m ₀ calc. mg.
0.1	2.2	2.2	200.	1050.	971.
5.0	48.0	50.8	300.	1360.	1340.
30.	212.	213.	400.	1660.	1690.
60.	376.	370.	500.	1930.	2020.
100.	580.	558.	1.0	14.	14.
r = 0.8			K = 7.14		

In the following tables, the "free space" is the volume, reduced to N.T.P., of helium or any other unadsorbable gas, required to fill the bulb containing the adsorbent at the equilibrium pressure.

V, the dead space of the adsorption bulb, is the total volume of the bulb minus the volume occupied by the adsorbent.

P₁ is the pressure which the gas admitted would exert if it occupied the dead space at the temperature of the experiment without being adsorbed.

TABLE IX⁹
Adsorption of Hydrogen on Platinum Black

m = 4.269 g.		V = 10.8 cc.		T = 25°C	
Gas admitted cc. at N.T.P.	Free space cc. at N.T.P.	P ₁ calc. mm. Hg.	P ₂ obs. mm. Hg	P ₂ calc. mm. Hg.	
17.34	10.00	1332.	768.	739.	
14.73	7.52	1131.	577.	551.	
12.27	5.15	942.	393.	377.	
9.10	2.13	699.	162.4	160.	
7.71	0.88	592.	67.8	71.	
6.94	.31	533.	23.5	25.	
6.07	.01	466.	1.1	—	
r = 0.9		1/r = 1.111		K = 3.628 × 10 ⁻⁵	
				R = 62350	

⁸ Lockeman and Lucius: Z. physik. Chem., 83, 743, Tables IV, VIII (1913).

⁹ Benton: J. Am. Chem. Soc., 48, 1859, Table II (1926).

TABLE X¹⁰
Adsorption Measurements on Platinized Gel

V = 29.3 cc.		m = 1 g.		T = 0°C	
Gas admitted cc. at N.T.P.	Free space cc. at N.T.P.	P ₁ calc. mm. Hg.	P ₂ obs. mm. Hg	P ₂ calc. mm. Hg	
2.70	1.31	70.0	34.00	31.9	
7.20	3.63	186.7	94.00	97.5	
15.20	8.25	394.2	214.00	225.	
24.80	14.35	643.3	372.00	386.	
35.68	20.60	925.5	553.00	573.	
46.17	28.40	1198.	735.70	759.	
Ethylene	r = 0.185	1/r = 5.4	K = 5.1 × 10 ⁻⁷		R = 62350
4.00	1.60	103.8	41.50	38.3	
9.60	4.07	249.0	105.50	110.	
16.50	7.63	428.0	197.50	208.	
26.50	13.55	687.2	351.45	360.	
42.75	23.35	1109.	604.50	618.	
Carbon Dioxide	r = 0.21	1/r = 4.76	K = 8.6 × 10 ⁻⁷		R = 62350
3.10	2.30	80.4	59.90	65.3	
7.50	6.24	194.6	161.50	161.	
14.75	13.15	382.5	340.50	321.	
22.00	19.70	570.5	509.50	480.	
31.90	28.70	827.4	743.00	702.	
Carbon Monoxide	r = 0.1	1/r = 10.	K = 5.6 × 10 ⁻⁸		R = 62350

The dead space in Tables IX and X was calculated by converting the free space to the corresponding equilibrium pressures and taking the average of the converted volumes.

Since x/m , in the reference from which the data in Table X was obtained, was seen to be the volume of gas admitted minus the free space value, m was assumed to be one gram.

In Tables IX and X, P_1 was calculated from "the gas admitted at N.T.P." by the perfect gas equation.

TABLE XI¹¹
Adsorption of Carbon Dioxide on Charcoal

V = 5.94 cc.		m = 4.5332 g.		T = 0°C	
P ₁ calc. mm. Hg	x/m cc./g.	P ₂ obs. mm. Hg	P ₂ calc. mm. Hg		
14360	24.6	90.4	—		
32470	55.3	399.4	385.		
38080	64.7	552.6	561.		
43530	73.8	734.0	762.		
48730	82.4	950.2	979.		
54330	91.6	1207.1	1237.		
58250	97.9	1478.2	1434.		
71943	119.1	2864.8	—		
r = 0.2		1/r = 5.	K = 3.616 × 10 ⁻⁷		R = 62350

¹⁰ Ryerson and Swearingen: J. Phys. Chem., 31, 96, Table V (1927).

TABLE XII¹¹
Adsorption of N₂O on Charcoal

V = 5.94 cc.		m = 4.5332 g.		T = 0°C	
P ₁ calc. mm. Hg	x/m cc./g.		P ₂ obs. mm. Hg	P ₂ calc. mm. Hg	
15194	26.0		61.5	—	
32220	55.1		262.6	255.	
37720	64.4		369.2	383.	
43130	73.5		504.3	533.	
48640	82.7		674.4	708.	
53370	90.5		881.4	877.	
58730	99.3		1138.4	1087.	
71623	118.6		2842.3	—	
r = 0.2		1/r = 5.	K = 3.804 × 10 ⁻⁷		R = 62350

The initial pressures in Tables XI and XII were calculated in the following manner. The volume which 5.94 cc. of gas at one of the observed equilibrium pressures would occupy at 760 mm. was calculated by the perfect gas equation. The value of x/m for the observation was multiplied by m . To this last volume was added the volume previously calculated. The pressure this total volume, which is at 760 mm., would exert if it occupied 5.94 cc. was calculated by the perfect gas equation. This pressure was P_1 .

The largest and smallest values of P_2 in the reference cited are given in Tables XI and XII. On examining the above data it is seen that the constants do not cover the entire range. But the constants do well to cover a range of 1000 mm. so efficiently when one makes allowance for the following facts: (a) the adsorption in Tables XI and XII is enormous, (b) equation (5) assumes a perfect gas, which is not the case for CO₂ and N₂O at the high pressures used at zero degrees, (c) P_1 is calculated from the available data on the assumption that CO₂ and N₂O are perfect gases.

Calculation of the Constants. From the method by which equations (1) and (4) were developed it would appear that $r = 1 - n$ and $K = (1 - n)k$, where n and k are the constants for the Freundlich adsorption isotherm. But this has been found not to be so. In order to find K and r one of the following procedures may be used. Equations for adsorption from liquids will be employed, but the procedures are similar for the adsorption of gases.

A. Equation (3) is $K = C_1^r V/m_0$. If C_1 is one then $K = V/m_0$. Thus, by experimentally determining the mass of adsorbent required to remove all the solute from a volume, V , of solution, K may be experimentally found. Now, if a single measurement is available in which C_1 is not one and C_2 is zero, then from equation (3) $r = \frac{\log (Km_0/V)}{\log C_1}$. Or, if a measurement is available in which C_1 is one and C_2 is not zero, then, from equation (2)

$$r = \frac{\log (1 - Km/V)}{\log C_2}.$$

¹¹ Richardson and Woodhouse: J. Am. Chem. Soc., 45, 2644, Table I (1923).

But a value of r obtained by one of the above methods is not usually efficient for the calculation of equilibrium values or m_0 . However, by retaining the value of $K = V/m_0$ and varying r in the region of the calculated value, an efficient value of r may be found. This procedure is permissible since r is an empirical constant.

B. If data of the kind required by the first method are not available, then the method of trial and error may be used with equation (1). Various values of r may be used with each set of measurements until the most constant value of K is obtained.

In Table VII, when C_1 equals one (1 mg./100 cc.), $K = V/m_0 = 100/13 = 7.7$. In the same manner, in Table VIII, $K = 7.14$. Using these values of K , values of r have been found for these tables which give good results. The data in these two tables, together with that in Table XIII, which are the results of an experiment carried out by the contributors of this article, indicate indubitably that $K = V/m_0$ when C_1 equals one.

TABLE XIII
Adsorption of NaOH in Water on Silica Gel
 $C_1 = 1.00$ centimols per liter in each case

V = 100 cc. in each case				
m obs. grams	C ₂ obs. cmols./l	C ₂ calc. cmols./l.	V(C ₁ - C ₂)/m obs cmols./g.	V(C ₁ - C ₂)/m calc. cmols./g.
2.0247	0.15	0.18	0.042	0.040
3.0210	.07	.06	.031	.031
4.1309	.03	.01	.024	.024
5.9941	.01	.0	.017	.017
6.0993	.0			

$$r = 0.24$$

$$1/r = 4.17$$

$$K = 16.4$$

The silica gel was used as supplied by the Silica Gel Corporation with no further treatment; it was 40 to 200 mesh. The usual precautions were taken to keep out CO₂ in all steps of the experiment. In seeking m_0 the masses of adsorbent were increased by approximately 0.1 gram because it was felt that the K so obtained would be sufficiently accurate. Because of the low concentrations, experimental and calculated values of $V(C_1 - C_2)/m$ as well as equilibrium concentrations are listed.

When C_1 is equal to one, $K = V/m_0$. K , therefore, is a measure of the adsorbability of the solute in that system to which the constant belongs.

From equation (3)

$$r = \frac{\log m_0 - \log m_0^1}{\log C_1 - \log C_1^1}$$

Therefore, r is the slope of the curve obtained by plotting $\log m_0$ against $\log C_1$.

Summary. An isotherm has been offered which describes adsorption from liquids and of gases. This isotherm contains a term for the initial concentration or pressure; it takes care of partial and total adsorption; it may be used to calculate equilibrium concentrations and pressures and the amount of adsorbent just required for total adsorption.

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March 26, 1932.*

CHLORINE EQUILIBRIA AND THE ABSOLUTE ENTROPY OF CHLORINE

BY A. R. GORDON AND COLIN BARNES

The modern interpretation of the structure of band spectra provides a direct means of calculating the entropies, specific heats and heats of dissociation of many gases. The numbers so obtained have been used successfully in calculating various thermodynamic quantities which are not immediately obtainable from experiment. In particular, equilibria in homogeneous gas reactions can be predicted in many instances with an accuracy which leaves little to be desired from the point of view of the chemist. It is probably only a matter of time and of increased knowledge of molecular spectra before the method is recognised as the most natural and accurate way of obtaining the characteristics of gaseous mixtures. The absolute entropies of many gases have now been calculated for fairly wide ranges of temperature, and the numbers so obtained can be used with a confidence impossible in dealing with "third law" values.

An entropy value for a gas, derived from its molecular spectrum, contains certain contributions which, in the calculation of an entropy of reaction, cancel identically with similar contributions to the entropies of other constituents; thus the presence of nuclear spins and, as will be shown below, the existence of isotopes lead to contributions of this nature. If it were only desired to calculate equilibrium constants, such terms in the entropies could be omitted from the beginning, and calculation correspondingly simplified; but to obtain entropies which may be designated *absolute*, every contribution suggested by the theory must be included. In this connection the effect of isotopes on an entropy calculation can be illustrated in the case of chlorine; although the isotopes are chemically indistinguishable, it will be shown that they are without thermodynamic significance only because of a peculiar compensation. In the present paper we shall compute the absolute entropy of molecular chlorine, and use the values so obtained to predict the equilibrium constant for the Deacon reaction.

1. The Entropy of Chlorine

According to Aston, the atomic weights of the isotopes Cl_{35} and Cl_{37} are 34.98 and 36.98 so that in ordinary chlorine they are present in the proportions 0.761:0.239; if it be assumed that for the temperature range involved the formation of a chlorine molecule is statistically determined by the relative abundance of the isotopes, then in ordinary chlorine the proportions must be $35\text{-}35\text{:}35\text{-}37\text{:}37\text{-}37 = 0.579\text{:}0.364\text{:}0.057$. The molar translational entropy S_T for a gas of molecular weight M at temperature T and pressure 1 atmosphere¹ is

$$S_T = -2.295 + 3R/2 \ln M + 5R/2 \ln T \quad (1)$$

¹ $R = 1.9858$; $k = 1.372 \times 10^{-16}$, $h = 6.55 \times 10^{-27}$.

At 300°K, S_T is 38.675, 38.759 and 38.841 for the three molecular varieties, respectively. The rotational or vibrational entropy is found in the usual way by

$$S = R(\Sigma_2/\Sigma_1) + R.\ln\Sigma_1 \quad (2)$$

where $\Sigma_1 = \sum p_n.e^{-\epsilon_n/kT}$, $\Sigma_2 = \sum p_n.(\epsilon_n/kT).e^{-\epsilon_n/kT}$

ϵ_n being the energy of the n 'th rotational or vibrational state of weight p_n . For temperatures above 300°, the rotational entropy assumes its classical value when the sums are evaluated:

$$S_R' = R + R.\ln 8\pi^2IkT/h^2 \quad (3)$$

where I is the moment of inertia of the diatomic molecule. It is known that Cl_{35} has 5/2 units of spin; the spin of Cl_{37} has not been determined, but we shall assume that it is the same as for Cl_{35} .¹ If this be the case, the spins of each type of molecule Cl_2 contribute a term $2R.\ln 6$ to the molar entropy. Now the 35-35 and 37-37 varieties are homonuclear, which means that (if it were not for nuclear spin) alternate rotational levels would be missing, i.e. a term $R \ln 2$ must be subtracted from S_R' in these two cases; no such correction is needed with the heteronuclear 35-37. Thus if S_R denote the contribution to the entropy from rotation and spins,

$$S_R(35-35, 37-37) = S_R'(35-35, 37-37) + 2R.\ln 6 - R.\ln 2$$

$$S_R(35-37) = S_R'(35-37) + 2R.\ln 6$$

The moments of inertia of 35-35 and 35-37 are 113.7×10^{-40} and 117.4×10^{-40} respectively,² and by simple proportion the moment of inertia for 37-37 is 121.1×10^{-40} . It is apparent from the work of Elliott,² however, that the moments of inertia increase by about 0.0070 of their values in the ground vibrational state per unit increase in the vibrational quantum number. In a molecule with as low a fundamental frequency as chlorine, this will introduce an appreciable error at high temperatures where the population of the higher vibrational states is large. A rough correction for this effect can be made by multiplying the numbers given above by $(1 + \Delta)$ where

$$\Delta = 0.0070(\Sigma n.e^{-\epsilon_n/kT})/(\Sigma e^{-\epsilon_n/kT})$$

in which ϵ_n is the energy of the n 'th vibrational state. Since $\Sigma_2/\Sigma_1 = \partial \ln \Sigma_1 / \partial \ln T$, this will introduce in the expression for the rotational entropy, a correcting term $s \approx 0.0070R(T.\partial \Delta / \partial T + \Delta)$. Including this correction,³ S_R for 35-35, 35-37 and 37-37 at 300° is 22.151, 22.591 and 21.275, respectively.

¹ If it should prove that Cl_{37} have a spin different from this, the change in the numbers obtained can be readily calculated; for example, if the spin should be 7/2 units instead of 5/2, the entropy of 37-37 will be increased by $2R \ln 8/6$ and that of 35-37 by $R \ln 8/6$ so that the numbers for ordinary chlorine in Table I will be increased by 0.273. The molar entropies of hydrogen chloride in the same Table will be increased by exactly half this amount.

² Elliott: Proc. Roy. Soc., 123A, 629 (1929); 127A, 638 (1930).

³ The numerical values of s are as follows:

T°K	300	400	500	600	700	800	900	1000
s	0.004	0.007	0.011	0.014	0.018	0.021	0.025	0.029

The vibrational energy levels are given by $\epsilon_n = (n + 1/2)\omega_0 - (n + 1/2)^2 \cdot b$ and the weights p_n are unity. Elliott² gives $\omega_0 = 564.9$ and $b = 4.0$ for 35-35; if it be assumed that ω_0 is inversely proportional to the square root of the reduced mass of the molecule, ω_0 for 35-37 and 37-37 will be 557.2 and 549.4, respectively. The vibrational entropy S_v for the three varieties is 0.545, 0.560 and 0.577 at 300°, so that the molar entropy at the same temperature is 60.37, 61.91 and 60.69. Therefore the entropy of one mole of chlorine at 300° is

$$0.579 \times 60.37 + 0.364 \times 61.91 + 0.057 \times 60.69 - 1.9858 (0.579 \ln 0.579 + 0.364 \ln 0.364 + 0.057 \ln 0.057) = 62.63$$

The last item ($= 1.683$) is the entropy of mixing. The values of the entropy and heat capacity of ordinary chlorine for various temperatures are listed in Table I; the vibrational part of the heat capacity was computed from the vibrational energy levels in the usual way, and a term $R \cdot \partial(T^2 \partial \Delta / \partial T) / \partial T$ was included to take into account the increase in the "average" moment of inertia through rise in temperature; the numerical value of this correction varies from 0.006 at 300° to 0.035 at 1000°.

2. The Entropies of Hydrogen Chloride and Oxygen up to 1000°

The translational entropy of HCl_{35} and HCl_{37} is given by Eq. 1 with $M = 35.99$ and 37.99 , giving for 300° $S_T = 36.695$ and 36.857 respectively. The rotational entropy is given by Eq. 2 with $\epsilon_J = J(J + 1)h^2/8\pi^2 I$, $p_J = 12$ ($2J + 1$), and $I = 2.617 \times 10^{-40}$ for both varieties;¹ the factor 12 in the weight arises from the spins of the hydrogen and chlorine atoms. For 300° $S_R = 12.852$. The vibrational entropy² is given by Eq. 2 with $p_n = 1$ and $\epsilon_n = n(2990 - 53.4n)$, where $n = 1/2, 3/2, \dots$. For 300° S_v is negligible and for 1000° is only 0.166, the isotope affect can be neglected in S_R and S_v . The entropy of ordinary hydrogen chloride as entered in Table I is given by

$$S = 0.761 S_{\text{HCl}_{35}} + 0.239 S_{\text{HCl}_{37}} - R(0.761 \ln 0.761 + 0.239 \ln 0.239)$$

the last term ($= 1.093$) being the entropy of mixing. If from the value for 300°, we subtract the spin entropy ($R \ln 12 = 4.935$) and the entropy of mixing, the result is 44.65, corresponding to 44.61 at 298°; Giauque and Wiebe³ give 44.64 for this temperature; the difference is exactly accounted for by our use of $R = 1.9858$ instead of $R = 1.9869$.

In the case of oxygen, Giauque and Johnston⁴ have computed the entropy for 298.1°; for higher temperatures, S_T is obtained from Eq. 1 with $M = 32.00$, S_R by setting⁵ $I = 19.27 \times 10^{-40}$ in Eq. 3 and then adding $R \ln 3/2$ to the result, while S_v is computed from Eq. 2 with $p_n = 1$ and $\epsilon_n = 1565n - 11.4n^2$ where $n = 0, 1, 2, 3, \dots$. Giauque and Johnston have shown that this method of

¹ Czerny: *Z. Physik*, **45**, 476 (1927).

² Kemble: *J. Opt. Soc. America*, **12**, 1 (1926).

³ Giauque and Wiebe: *J. Am. Chem. Soc.*, **50**, 101 (1928).

⁴ Giauque and Johnston: *J. Am. Chem. Soc.*, **51**, 2300 (1929).

⁵ Dieke and Babcock: *Proc. Nat. Acad. Sci.*, **13**, 670 (1927); Rasetti: *Phys. Rev.*, (2) **34**, 367 (1929); Birge: *Int. Crit. Tables* **5**, 411.

approximation leads to the same numerical result at 298.1° as their more exact method based on the band spectrum formula for oxygen. The resulting values for the entropy and heat capacity are entered in Table I; for 298.1° the entropy is 49.00, which is 0.03 less than Giauque and Johnston's value; as in the case of hydrogen chloride, this discrepancy is exactly accounted for by our use of a smaller value of R.

TABLE I

Molar Entropies and Heat Capacities of Chlorine, Hydrogen Chloride and Oxygen

T°K	Chlorine		Hydrogen Chloride		Oxygen	
	S	C _p	S	C _p	S	C _p
300	62.63	8.12	50.68	6.95	49.04	7.02
400	65.02	8.43	52.68	6.96	51.08	7.19
500	66.92	8.62	54.23	6.99	52.71	7.42
600	68.50	8.73	55.51	7.05	54.09	7.65
700	69.85	8.81	56.61	7.14	55.28	7.86
800	71.03	8.87	57.57	7.26	56.34	8.03
900	72.08	8.91	58.43	7.39	57.30	8.17
1000	73.02	8.94	59.21	7.52	58.17	8.29

3. The Deacon Equilibrium $2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2$

If Q be the heat of reaction at temperature T and if ΣS be defined by

$$\Sigma S = 2S_{\text{Cl}_2} + 2S_{\text{H}_2\text{O}} - 4S_{\text{HCl}} - S_{\text{O}_2}$$

the entropies being all for temperature T and pressure 1 atmosphere, then at equilibrium

$$R \ln K = R \ln (P_{\text{Cl}_2})^2 (P_{\text{H}_2\text{O}})^2 / (P_{\text{HCl}})^4 (P_{\text{O}_2}) = -Q/T + \Sigma S$$

The heat of formation of hydrogen chloride¹ at 291° is 22030 cal.; the heat of formation of water² at 298° is 68313 cal. and the heat of vaporization at the same temperature⁴ is 10485 cal.; hence at 298° , $Q = -27,500$ cal. From this value, and the heat capacities of steam⁴ and the other gases (Table I), the values of Q/T entered in Table II are found by tabular integration. ΣS , entered in the same table, is obtained from Table I above and from the known entropy of steam.⁴ The resulting $R \ln K$ were used to construct the curve in Fig. 1; the experimental values of this quantity, as obtained from International Critical Tables,⁵ together with some additional experimental results of von Falkenstein⁶ and Neumann⁷ are indicated on the figure. The following values are suggested for the reaction:

$$\Delta H^\circ_{298.1} = 27,500; \Delta S^\circ_{298.1} = 30.99; \Delta F^\circ_{298.1} = 18260.$$

¹ Int. Crit. Tables, 5, 176.

² Rossini: Bur. Standards J. Research, (6) 1, 36 (1931).

³ Int. Crit. Tables, 5, 138.

⁴ Gordon and Barnes: J. Phys. Chem., 36, 1143 (1932).

⁵ Int. Crit. Tables, 7, 233.

⁶ von Falkenstein: Z. physik. Chem., 65, 371 (1909).

⁷ Neumann: Z. angew. Chem., 28, 233 (1915).

TABLE II
The Equilibrium Constant for the Deacon Reaction

T°K	600	700	800	900	1000
$-Q/T$	46.70	40.17	35.27	31.46	28.42
$-S$	32.21	32.40	32.52	32.60	32.71
$R \ln K$	+14.49	+7.77	+2.75	-1.14	-4.29

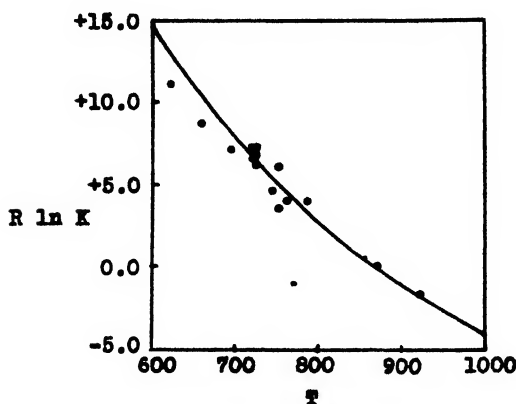


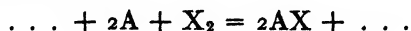
FIG. 1

4. Isotopes in Entropy Calculations

The entropy values of chlorine and hydrogen chloride as derived in Sec. 1 and 2 may be used to illustrate the general question of the effect of isotopes on an entropy calculation. Earlier calculations of the entropy of these two gases ignored the existence of isotopes in chlorine, and it is important to show the effect of this on the numbers obtained. To a first approximation, we may disregard the effect of isotopes on the values of S_R and S_V , and consider S_T as a linear function of the molecular mass M . With isotopes considered in chlorine, there occurs an entropy of mixing of 1.683, which is absent when these are disregarded. In addition, in a non-isotopic chlorine, all molecules would be homonuclear, and the extra entropy due to the heteronuclear nature of 35-37, viz. $0.364R \ln 2$, would not be present in the final entropy expression. Thus to ignore the existence of isotopes is to decrease the entropy of chlorine by $1.683 + 0.364R \ln 2 = 2.18$. If for non-isotopic chlorine $M = 70.92$, $I = 116 \times 10^{-40}$, and $\omega_0 = 560 \text{ cm}^{-1}$, the entropy can be readily evaluated and is found to be (at 300°) 60.46, which is just 2.17 less than the number in Table I. Now to disregard the chlorine isotopes in hydrogen chloride is practically equivalent to dropping the entropy of mixing, viz. 1.093, so that as far as the calculation of ΔS for the Deacon reaction is concerned, the effect of the isotopes cancels.

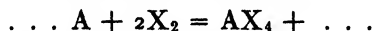
By writing down the general expression for the entropy of mixing for a diatomic gas X_2 having any number of isotopes in any relative proportions, and taking account of the $-R \ln 2$ which will occur in the molar entropy of

any homonuclear combination, we can get the extra entropy due to isotopes. If we compare this with the entropy of mixing for molecules of the type AX, then in any reaction of the type



ΔS for the reaction is the same (to a first approximation) whether we consider the presence of isotopes or disregard them. Of course the temperature must always be so high that the rotational energy is classical (Eq. 3).

The indifference of ΔS to isotopes appears to be general, as would be expected for chemical reasons. The above type of cancellation can be shown to take place, for example, in the reaction



For simplicity, suppose that X has two isotopes X' and X'' in the relative proportions $\alpha, \beta = 1 - \alpha$. Then the entropy due to isotopes on the left hand side of the reaction is

$$\begin{aligned} & - 2R[\alpha^2 \ln \alpha^2 + \beta^2 \ln \beta^2 + 2\alpha\beta \ln 2\alpha\beta] + 4R\alpha\beta \ln 2 \\ & = - 4R(\alpha \ln \alpha + \beta \ln \beta). \end{aligned}$$

Now if AX_4 has the symmetry properties of methane, as may be assumed for the illustration, there is the following distribution of molecular types

Type	Proportion	Symmetry Number
AX_4'	α^4	12
$AX_3'X''$	$4\alpha^3\beta$	3
$AX_2'X_2''$	$6\alpha^2\beta^2$	2
$AX'X_3''$	$4\alpha\beta^3$	3
AX_4''	β^4	12

The column headed "Symmetry Number" determines the correcting term to be taken from the classical entropy expression to allow for the absence of a certain fraction of the energy states. Thus the symmetry number for the homonuclear varieties of chlorine is 2, and $R \ln 2$ is to be subtracted from S_R' in Eq. 3; similarly the entropy of a mole of $AX_2'X_2''$ will be $R \ln 12/2$ greater than that of a mole of AX_4' or AX_4'' , and so on. Therefore, the isotope entropy on the right hand side of the reaction in question is

$$\begin{aligned} & - R[\alpha^4 \ln \alpha^4 + 4\alpha^3\beta \ln 4\alpha^3\beta + 6\alpha^2\beta^2 \ln 6\alpha^2\beta^2 + 4\beta\alpha^3 \ln 4\alpha\beta^3 + \beta^4 \ln \beta^4] \\ & + R[4\alpha^3\beta \ln 4 + 6\alpha^2\beta^2 \ln 6 + 4\alpha\beta^3 \ln 4] \\ & = - 4R(\alpha \ln \alpha + \beta \ln \beta). \end{aligned}$$

This latter quantity is identical with that obtained for the left-hand side of the reaction.

Of course, one cannot assert that this type of cancellation will necessarily take place in every reaction, since the "symmetry number" is known for only the simplest types of molecules; in all the simple cases that can be treated by the method sketched above, however, it is found that the part due to mixing

together with the part due to "symmetry" gives, on either side of the reaction, the same numerical result. To this extent, then, the effect of isotopes may be disregarded in questions of chemical equilibrium. The compensation is not exact, of course, for the mass effect of the isotopes has been disregarded, and this in general will not cancel, e.g. in the terms S_V of the entropies; this is a "second order" effect, however, amounting to (at most) a few hundredths of an entropy unit in the entropy of reaction.

Summary

The entropy of chlorine from 300° to 1000° is computed from the spectroscopic constants of Elliott; in conjunction with the known entropies of hydrogen chloride, oxygen and steam, the equilibrium constant of the Deacon reaction is calculated for the range 600° - 1000° . The agreement between the calculated and observed values of the equilibrium constant is satisfactory. It is shown that to the first order, the entropy of reaction is not affected by disregarding the existence of isotopes in the calculation; the rule appears to be general.

Added in proof, June 28, 1932: Since this paper was sent to the Journal, Giaque and Overstreet (J. Am. Chem. Soc., **54**, 1731 (1932)) have computed the entropy of chlorine by a method which takes exact account of the change in the spectroscopic constants in the higher rotational-vibrational states; they find 53.310 as the entropy of chlorine at 298.1° . If from our value at 300° , the spin entropy (7.116) and the isotope entropy (2.186) be subtracted, the result is 53.33, corresponding to 53.28 at 298.1° ; with $R = 1.9869$, this last value becomes 53.31. A calculation by their method for 1000° shows that the entry in Table I is less than 0.02 in error.

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Toronto, Canada.
April, 1932.*

PHASE RULE STUDIES ON THE PROTEINS. VII*

Non-aqueous Solutions

BY WILDER D. BANCROFT AND S. LOUISA RIDGWAY

Introduction

In a recent paper¹ the authors came to these conclusions: "Casein, gelatine and edestin showed compound formation with HCl in ethyl alcohol. Zein and gliadin showed only adsorption with HCl. Casein, gelatine, zein, gliadin and edestin showed compound formation with NaOH in ethyl alcohol plus marked adsorption, or adsorption alone with the adsorption practically complete at the lower concentrations." The method used in obtaining these results was briefly this. The protein was put in a given volume of the solvent, which was assumed to be inert to the system, containing the requisite amount of acid or base; after equilibrium had been attained, the excess acid or base was titrated using such indicators that any peptized protein or protein product would have no effect on the end-point. The practical difficulties involved in interpreting the curves obtained were pointed out. These were: (1) such complete adsorption that a flat appeared to be obtained; (2) lack of equilibrium in compound formation simulating an adsorption curve; and (3) change in the shape of the curve due to hydrolysis of the protein during the time required to reach equilibrium.

The object of the paper quoted was to determine whether proteins form adsorption complexes or true compounds with acids and bases. This has also been the object of the present research. A modification of the method previously used seemed to obviate some of the difficulties just mentioned. If the protein could be dissolved without chemical change in a small amount of some solvent and then poured into a large amount of a second solvent, in which the protein is insoluble, containing the acid or base, the protein would be precipitated in very small particles and equilibrium ought to be reached rapidly. The excess acid or base could be titrated very soon and there would be less chance for hydrolysis of the protein. Aside from the theoretical importance of this modification, the saving of time in experimental work would be enormous. The simplest example (and the only one actually used so far) is that of gelatine dissolved in water and poured into alcohol. The method is limited to proteins soluble in some medium which does not change them chemically—for instance gelatine and albumin in water, and the prolines in alcohol-water mixtures.

¹ J. Phys. Chem., **36**, 1285 (1932).

*This work has been done under the programme now being carried out by Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

Experimental

The experimental method was extremely simple. A gram of gelatine was dissolved in 10 cc. of warm water in a test tube, and the resulting solution was poured into a flask containing the desired amount of acid or base dissolved in 90 cc. of absolute alcohol. The test tube had been passed through a rubber stopper fitting the flask, so that the liquid could easily be shaken from one to the other. The gelatine precipitated as soon as it was poured into the alcohol, and in a short time agglomerated into one mass. In spite of this it

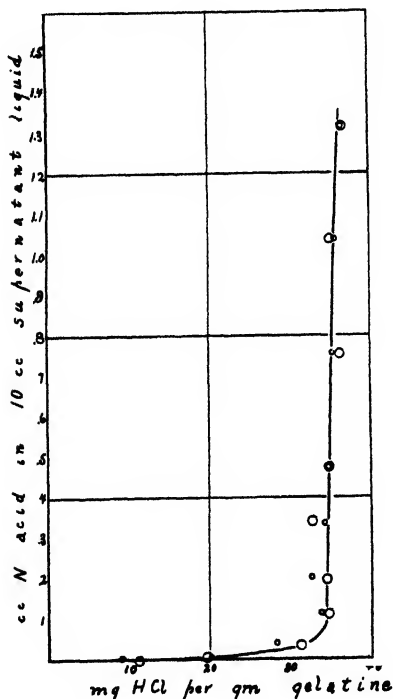


FIG. 1

Gelatine and HCl in 90% Ethyl alcohol
 o = 0°C. O = Room Temperature

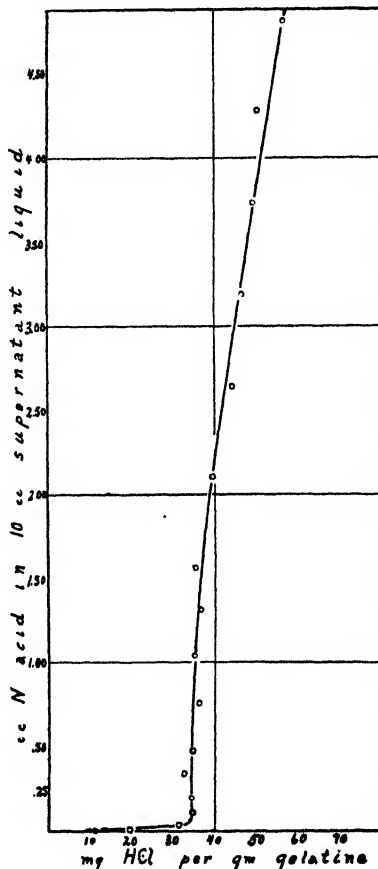


FIG. 2

Gelatine and HCl in 90% Ethyl Alcohol
 High Acid Concentrations

seemed that equilibrium was reached very rapidly. After an hour or more an aliquot portion of the supernatant liquid was pipetted off and titrated for excess acid or base using standard base or acid in 95% alcohol. The red to yellow change of thymol blue was used to titrate excess acid, and thymolphthalein was used for excess base. Only strong acid or base was titrated by this method. The results of the titrations were corrected for the volume change incident to the mixing of water and alcohol. Some titrations were

made at 0°C . and the results of these were also corrected for the volume change due to temperature.

The amount of acid or base left in a definite volume of supernatant liquid was plotted against the amount used by a gram of dry protein. In the interpretation of the curves, the same principles used in the previous method were applied. A constant concentration of the supernatant liquid with varying

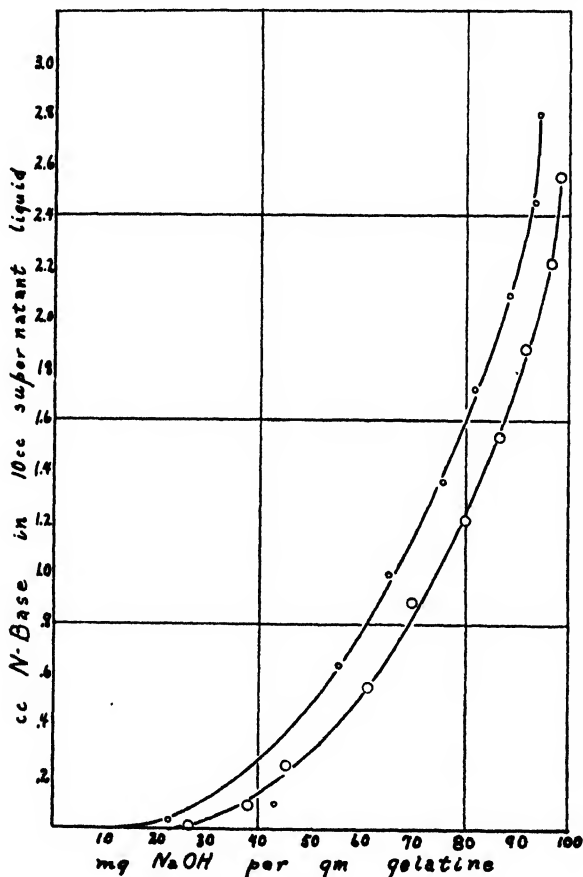


FIG. 3

Gelatine and NaOH in 90% Ethyl Alcohol
 o = 0°C . O = Room Temperature

values of the amount taken up indicated compound formation, while continuously varying values of both indicated adsorption.

The first runs were made with HCl on the gelatine used in the earlier work. That particular lot of gelatine was exhausted before the new method was quite perfected and therefore no data are given. The results are important only because they are substantially the same as those obtained by the old method, and show the equivalence of the two.

The rest of the work was done on a sample of ash-free gelatine obtained from the Eastman Company. Runs were made with HCl at room tempera-

ture and at 0°C. A set of typical data for each are given in Tables I and II and plotted in Fig. 1. The data for a run made at higher acid concentrations is given in Table III and plotted, together with the data from Table I, in Fig. 2.

Single runs were made with NaOH at room temperature and at 0°C. The results are given in Tables IV and V, and plotted in Fig. 3.

TABLE I

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each run = 98.7 cc. Length of run = 2 hours.

Room temperature or approximately 25°C.

a = cc N HCl added; b = cc N base for 50 cc supernatant liquid; c = cc N acid in supernatant liquid = $b \times 1.974$; d = cc N acid in 10 cc supernatant liquid = $b/5$; e = cc N acid used per g gelatine equivalent $\times 10^{-3}$ $(a-c)/0.891$; f = mg HCl per g gelatine = $e \times 36.468$.

a	b	c	d	e	f
0.28	0.00	0.00	0.00	0.31	11.4
0.56	0.04	0.07	0.01	0.54	19.7
1.11	0.17	0.34	0.04	0.86	31.4
1.94	0.55	1.09	0.11	0.95	34.8
2.78	0.98	1.93	0.20	0.95	34.5
4.17	1.70	3.36	0.34	0.90	32.8
5.55	2.38	4.70	0.48	0.96	34.0
8.33	3.77	7.44	0.75	1.00	36.4
11.11	5.19	10.25	1.04	0.96	35.0
13.89	6.58	12.99	1.32	1.01	36.8

TABLE II

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of runs 1-3 = 100 cc.; volumes of numbers 4-10 = 98.7 cc. Temperature = 0°C.

Length of run = $1\frac{1}{2}$ hours.

a = cc N HCl added; b = cc N base for 50 cc supernatant liquid (cold); C = cc N acid in supernatant liquid = $(b \times \text{vol})/51$; d = cc N acid in 10 cc supernatant liquid = $b/5.1$; e = cc N acid used per g gelatine equivalent $\times 10^{-3}$ = $(a - c)/0.891$; f = mg HCl per g gelatine = $e \times 36.468$.

a	b	c	d	e	f
0.28	0.02	0.04	0.004	0.26	9.3
0.56	0.03	0.06	0.006	0.56	20.3
1.11	0.21	0.42	0.04	0.78	28.3
1.95	0.58	1.12	0.11	0.93	33.8
2.78	1.02	1.98	0.20	0.90	32.6
4.17	1.72	3.33	0.34	0.94	34.3
5.56	2.43	4.71	0.48	0.96	34.8
8.33	3.86	7.47	0.76	0.97	35.4
11.11	5.29	10.24	1.04	0.98	35.7
13.89	6.72	12.99	1.32	1.01	36.7

TABLE III

Gelatine and HCl in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = 2 hours.

Room temperature = about 25°C.

a = cc N HCl added; b = cc N base for 50 cc supernatant liquid; c = cc N acid in supernatant liquid = $b \times 2$; d = cc N acid in 10 cc supernatant liquid = $b/5$; e = cc N acid used per g gelatine equivalent $\times 10^{-3} = (a - c)/0.891$; f = mg HCl per g gelatine = $e \times 36.468$.

a	b	c	d	e	f
16.49	7.81	15.63	1.56	0.97	35.4
21.99	10.51	21.02	2.10	1.09	39.8
27.49	13.21	26.41	2.64	1.21	44.3
32.98	15.92	31.84	3.18	1.28	46.7
38.48	18.64	37.28	3.73	1.35	49.4
43.98	21.38	42.75	4.28	1.38	50.2
49.48	24.04	48.09	4.81	1.46	56.9

TABLE IV

Gelatine and NaOH in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = 2½ hours.

Room temperature = about 25°C.

a = cc N NaOH added; b = cc N acid for 50 cc in supernatant liquid; c = cc N base in supernatant liquid = $b \times 2$; d = cc N base in 10 cc supernatant liquid = $b/5$; e = cc N base used per g gelatine equivalent $\times 10^{-3} = (a - c)/0.891$; f = mg NaOH per g gelatine = $e \times 40.008$.

a	b	c	d	e	f
0.69	0.05	0.10	0.01	0.66	26.6
1.73	0.44	0.88	0.09	0.95	38.0
3.46	1.22	2.45	0.25	1.14	45.4
6.92	2.78	5.55	0.56	1.54	61.2
10.37	4.41	8.82	0.88	1.74	69.7
13.83	6.03	12.05	1.21	2.00	80.0
17.29	7.68	15.36	1.54	2.17	86.8
20.75	9.36	18.73	1.87	2.27	90.7
24.21	11.03	22.06	2.21	2.41	96.6
27.66	12.74	25.48	2.55	2.46	98.2

TABLE V

Gelatine and NaOH in 90% Ethyl Alcohol

1 g gelatine, equivalent to 0.891 g dry gelatine, used in each run. Volume of each number = 100 cc. Length of run = $3\frac{1}{2}$ hours.

Temperature = 0°C.

a = cc N NaOH added; b = cc N acid for 50 cc supernatant liquid (cold); c = cc N base in supernatant liquid = $(b \times 100)/51$; d = cc N base in 10 cc supernatant liquid = $b/5.1$; e = cc N base used per g gelatine equivalent $\times 10^{-3} = (a - c)/0.891$; f = mg NaOH per g gelatine = $e \times 40.008$.

a	b	c	d	e	f
0.76	0.13	0.26	0.03	0.57	22.7
1.90	0.48	0.94	0.09	1.08	43.1
3.81	1.59	3.13	0.31	0.76	30.5
7.61	3.25	6.37	0.64	1.39	55.7
11.42	5.08	9.96	0.99	1.63	65.1
15.22	6.90	13.53	1.35	1.90	75.8
19.03	8.77	17.20	1.72	2.05	81.9
22.83	10.64	20.85	2.09	2.22	88.6
26.64	12.52	24.55	2.46	2.34	93.6
30.06	14.40	27.95	2.80	2.36	94.4

Discussion

The form of the curve obtained with HCl strongly suggests that a compound is formed, for it has two distinct portions with a fairly sharp break between them. It would be more conclusive if the "flat" really were flat instead of showing a very gradually increasing concentration of acid in the supernatant liquid. This may be due to a correspondingly small amount of hydrolysis of the assumed compound. If it is an adsorption phenomenon which is taking place, there should be more acid taken up by the protein at 0°C. than at room temperature for adsorption has a negative temperature coefficient. The curves are identical within experimental error, so that this is negative evidence for compound formation. Considering the whole evidence, we must return to our original conclusion that gelatine forms a compound with HCl in ethyl alcohol. At higher concentrations of acid, there is some adsorption on the compound formed. We predict that there would be increased adsorption at 0°C.

This sample of gelatine combined with somewhat more acid than the preceding one. The compound contained 92×10^{-5} equivalents or 33.5 mg. of HCl per gm. of dry gelatine, thus giving the gelatine a combining weight of 1090. This agrees well with much other work done on gelatine and HCl in water solution.¹ The other sample bound 86×10^{-5} equivalents.

¹ Bancroft and Ridgway: J. Phys. Chem., 36, 1311 (1932).

The curves with NaOH are typical adsorption curves. Theoretically the run at 0°C. should show more adsorption of NaOH, while the opposite is true. At present we have no explanation for this.

Conclusions

1. A new method for studying the acid and base binding power of certain proteins in non-aqueous solvents has been given.
2. Gelatine forms a compound with HCl in ethyl alcohol.
3. Gelatine probably adsorbs NaOH from ethyl alcohol without any compound formation.

Cornell University.

THE SORPTION OF ALCOHOL VAPORS BY CELLULOSE AND CELLULOSE ACETATES*†

BY S. E. SHEPPARD AND P. T. NEWSOME

The present paper deals with (a) the sorption equilibria of various alcohols with cellulose and cellulose acetates, (b) the rates of adsorption and desorption of alcohols by cellulose and cellulose acetates under definite conditions and (c) deductions regarding the sorption process and the fine and coarse structure of cellulose materials.

All measurements were made with an enclosed silica spring balance at 30°C. The cellulose materials used consisted of a series of primary and secondary acetates—primary acetates, extending from pure cotton linters (0% acetyl) to cellulose triacetate (44.8% acetyl), and secondary (hydrolyzed) acetates decreasing from 44.8% acetyl to 35.5% acetyl. As will be shown later, it is necessary to distinguish between adsorption by the “native” and by the “hydrate” crystalline forms of the various cellulose materials.

The secondary acetates all possess the “hydrate” form and the primary acetates are more or less converted from the “native” form of the original cotton linters to the “hydrate” form depending on the degree of dispersion in the acetylating mixture (the permanent conversion to hydrate form is probably complete above 40% acetyl).

Conversion to the hydrate form, expanded crystal lattice, results in an increased adsorbing capacity of pure cellulose and cellulose derivatives, as indicated by moisture adsorption experiments (see “The Sorption of Water Vapor by Cellulose and its Derivatives,” Part I.¹). The same result is also shown by the following alcohol adsorption data.

The relative rates of adsorption of methyl and ethyl alcohol vapors at the saturation pressure at 30°C. are independent of the acetyl content, although the maximum adsorption varies greatly with the acetyl content (see Figs. 1 and 2). However, the relative rates of adsorption of n-propyl and n-butyl alcohol vapors are definitely lower for the higher acetates (see Figs. 3 and 4). This indicates the existence of a difference in structure between the different acetates which was not apparent in the methyl and ethyl alcohol adsorption curves. A further discussion of this point will be given later in this paper.

In general, the rate of adsorption of alcohol vapor by any primary, or secondary acetate decreases as we go up the alcohol series (see Figs. 1, 2, 3 and 4). The difference in the rate of adsorption of water and various alcohols up to n-octyl alcohol by a secondary acetate (38% acetyl) is shown in Fig. 5. Higher alcohols are adsorbed more slowly than the lower alcohols because of lower vapor pressure and greater molecular size.

* Presented at American Chemical Society Meeting, Buffalo, August, 1931.

† Communication No. 494 from the Kodak Research Laboratories.

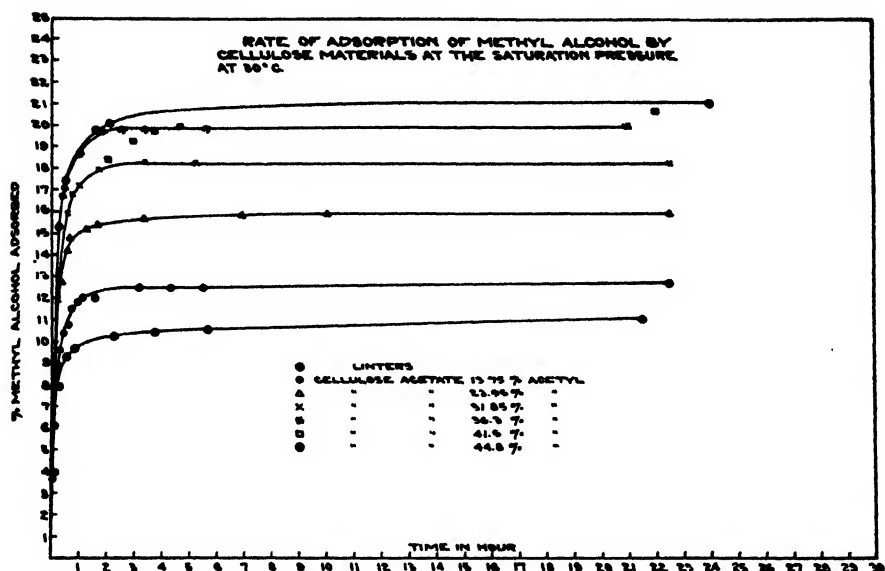


FIG. 1

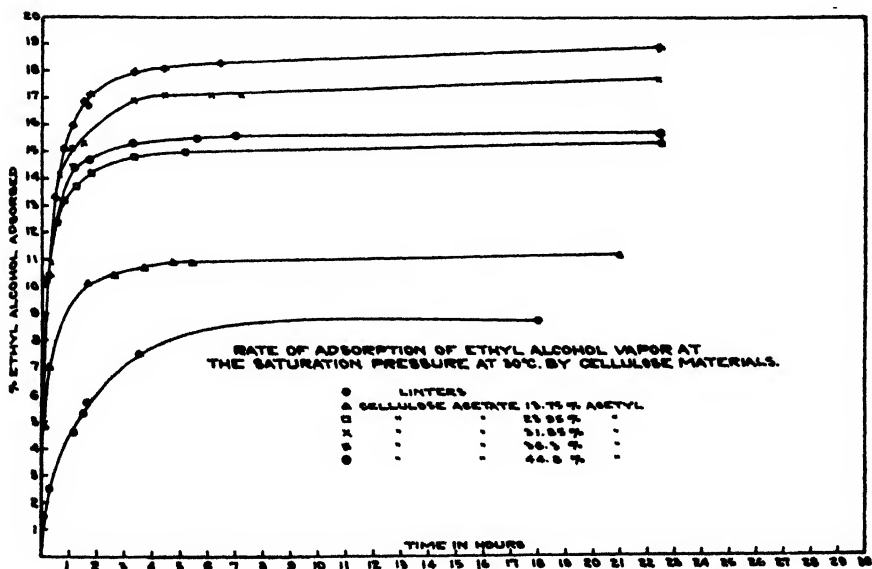


FIG. 2

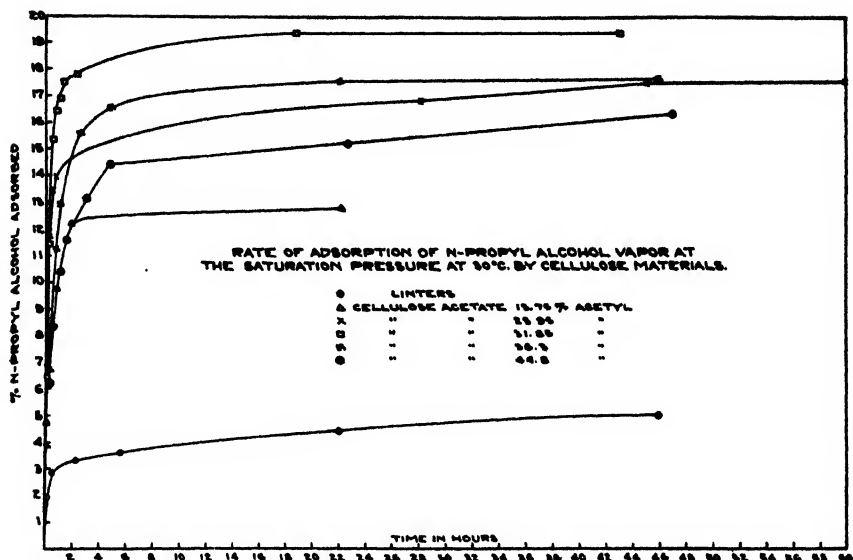


FIG. 3

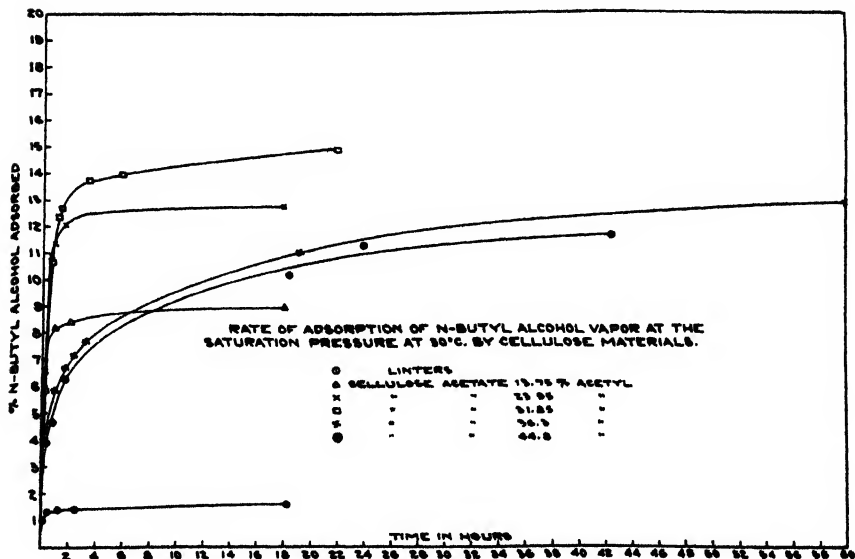


FIG. 4

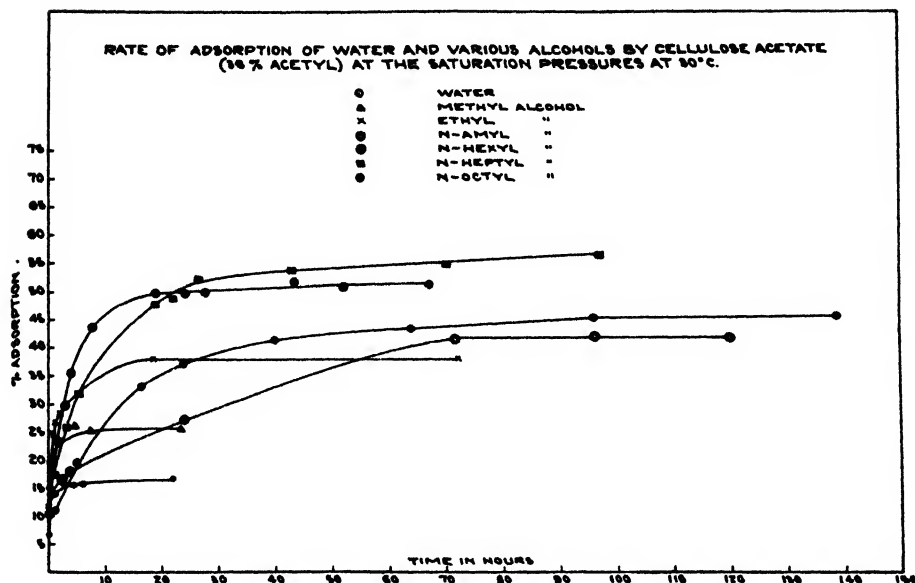


FIG. 5

The difficulty of maintaining a saturated atmosphere about the adsorbent increases with increasing molecular weight and lower vapor pressure of the alcohol. This is very important in a comparative study of adsorption rates at the saturation pressures. The rate of adsorption of the higher alcohols varies greatly depending on the shape of the apparatus even in the absence of air. Molecules of the higher alcohols diffuse slowly through long lengths of connection tubing. In all of the measurements recorded here the adsorbent was suspended from a silica spring balance in an air-free system not over 3 cm. above an area of 7 sq. cm. of liquid and the saturation pressure if known, was maintained as observed with a manometer.

Figs. 6 and 7 show the maximum adsorptions at the saturation pressures at 30°C. of water and alcohol vapors in per cent of the original dry weight and also in moles of the initially dry materials. The arrows in the figures indicate the direction of changing acetyl content (up to the triacetate and down again by hydrolysis).

The variation of maximum adsorption with acetyl content shown in Fig. 1 can logically be carried only as far as 41.5% acetyl, since the triacetate and three secondary acetates do not belong to the same series—the latter data are included in order to show the variation in adsorption of the different vapors by the same acetate. Nevertheless, it is clear that secondary acetates have a much greater adsorbing capacity for water and alcohol vapors than primary acetates of the same acetyl content.

The data of Fig. 7 show the variation in adsorbing capacity of a series of acetates all from the same batch. The water adsorption falls continuously

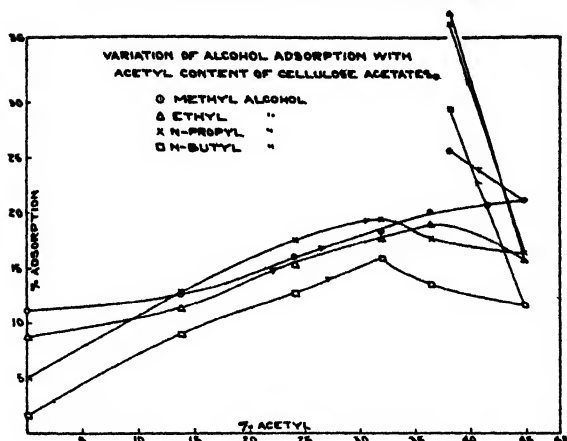


FIG. 6

with increasing acetyl content. The methyl and ethyl alcohol adsorptions rise continuously with increasing acetyl content while *n*-propyl and *n*-butyl alcohol adsorptions show maxima at 31.8% acetyl.

Werner and Engelmann² measured the adsorption of ethyl alcohol by sheets of cellulose (cellophane) and cellulose acetates when immersed in a solution of alcohol with 10% ether. A maximum adsorption was found at 37.7% acetyl. They also observed that the amount of water retained by the various sheets when immersed in liquid water and blotted dry decreased directly as the acetyl content increased from 0 to 44.8% acetyl. This is in fair agreement with our results on the sorption of water vapor by different cellulose acetates.³ They point out relations between the variation of adsorption and solubility with acetyl content.

The amount of alcohol adsorbed by primary acetates, when expressed as moles per gram of dry material, decreases continuously in going up the alcohol series from methyl to *n*-butyl. But when the same adsorption is

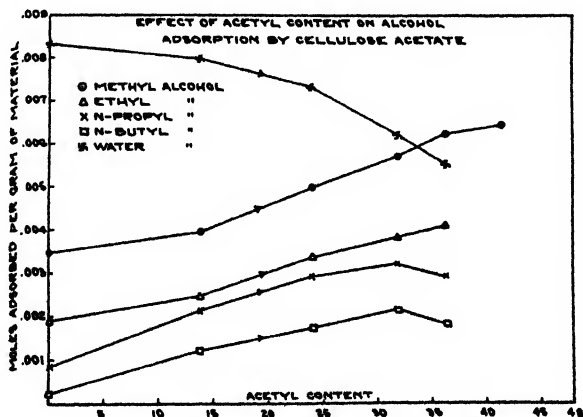


FIG. 7

expressed as per cent of the dry weight, this is not true because certain acetates adsorb more n-propyl alcohol than either methyl or ethyl alcohols (compare Figs. 6 and 7). Approximately 50% of adsorbed water appears to be held by hydroxyl groups in pure cellulose and any decrease in hydroxyl content produced by acetylation results in a decreased moisture adsorption. But the alcohols, also possessing polar hydroxyls, behave quite differently. A decrease in hydroxyls occasioned by acetylation results in an increased adsorption of alcohols by primary acetates, except for n-propyl and n-butyl, by acetates containing more than 32% acetyl. This behavior of the alcohols cannot be

attributed to any gradual change of fine structure from native to hydrate form since both native and hydrate forms give, in general, the same results. (Compare our results with the native form to those of Werner and Engelmann using the hydrate form.) Neither is it entirely true that alcohols are held more strongly by acetate groups than by hydroxyls, since n-propyl and n-butyl alcohols show the reverse above 32% acetyl. Our results⁴ show that increased dispersion as indicated by different viscosities does not increase the adsorbing capacity, since regenerated celluloses of low viscosity absorb less water than mercerized cellulose of high viscosity. However, Pringsheim, Kusenack and Weinreb⁵ have found that the acetylation of cellulose, employing zinc chloride as catalyst, is accompanied by a decrease in particle size and that the conversion of primary triacetate into acetone-soluble secondary acetate involves a further disaggregation and theoretically, increased solubility in a given solvent will always be accompanied by increased adsorbability of the vapor of that solvent. Our results agree with this in that secondary acetates adsorb alcohols as well as water more strongly than primary acetates.

Further measurements on the adsorption of different alcohols by cellulose materials of different crystalline structure, viscosity, chemical constitution, and external dispersity are necessary in order to clarify the problem. Such a study may also give an explanation of the wide divergence which has been found in the moisture regain of both dope and fibrous acetylated cellulose triacetates.

Fig. 8 and Table I show the adsorption of the saturated normal alcohols up to and including n-octyl by the same secondary acetate (38% acetyl). The molar adsorbing capacity of this acetate, contrary to the behavior of primary acetates, does not fall in a regular manner as we go to the higher alcohols. However, as an approximation, the molar adsorption falls rapidly from water with no carbon atoms to butyl alcohol with four carbon atoms and then re-

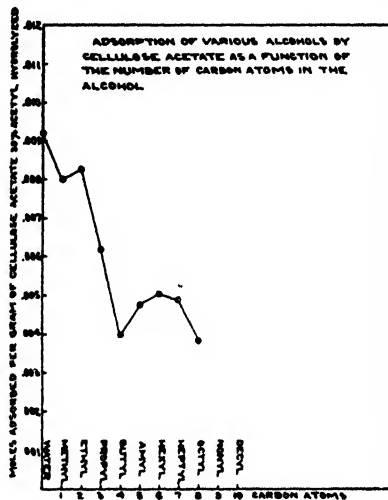


FIG. 8

mains constant at a value of 0.004 to 0.005 moles per gram of acetate. This behavior might be expected if we assumed that butyl alcohol just ceased to penetrate the cellulose units, and that from this alcohol onward, we have pure surface adsorption with the hydroxyls of the alcohols attached to the cellulose. Since the cross section of the alcohols remains the same with increasing number of carbon atoms, the molar adsorption would also remain constant, assuming uniformity of exposed surface and complete covering by the alcohols with the formation of a unimolecular layer.

A calculation of the total adsorbing surface of a gram of cellulose acetate may be made as follows:

According to N. K. Adam⁶ the area occupied by the $-\text{CH}_2\text{OH}$ group when oriented on a surface is 21.7×10^{-18} sq. cm. Since we have 0.0045 moles of adsorbed alcohol, the total area occupied is $0.0045 \times 6.06 \times 10^{23} \times 21.7 \times 10^{-18} = 5,918,000$ sq. cm. per gram.

TABLE I

Adsorption of Various Vapors at Their Saturation Pressures at 30°C. by the same Cellulose Acetate (Hydrolyzed—38% acetyl)

Vapor	Boiling Point °C	V.P. mm. Hg. at 30°C	Mol. Wt.	% Adsorption per gram	Moles Absorbed per gram	Moles per Gram V.P.
Methyl alcohol	64.5	160.0	32.03	25.6	0.0080	0.00005
Ethyl alcohol	78.5	78.8	46.05	38.1	0.00827	0.000105
n-Propyl alcohol	97.8	27.6	60.06	37.2	0.00618	0.000224
n-Butyl alcohol	117.7	9.5	74.08	29.4	0.00397	0.000417
n-Amyl alcohol	137.9	5.5	88.10	41.9	0.00476	0.000858
n-Hexyl alcohol	155.8		102.11	51.5	0.00504	
n-Heptyl alcohol	175.8		116.12	56.8	0.00489	
n-Octyl alcohol	194		130.14	50.1	0.00385	
Water	100	31.82	18.02	16.5	0.00918	0.000288
Acetic Acid	118.1	20.6	60.03	144.9	0.02615	0.00127

From a consideration of compression forces and thickness of adsorbed water layer Stamm⁷ calculated the total adsorbing surface of wood material to be 310,000 sq. cm. per gram. The above value for cellulose acetate is probably high because of some formation of polymolecular layers of adsorbed alcohol.

The last column of Table I shows the adsorption in moles per gram of cellulose acetate divided by the vapor pressure of the adsorbate. The vapor pressures of n-hexyl, n-heptyl and n-octyl alcohols were not available. From methyl to amyl alcohols the above quantity doubles for each additional CH_2 group. The maximum adsorption at the saturation pressure at any temperature is independent of the absolute value of the vapor pressure of the liquid under consideration. The energy changes involved are dependent only on the relative vapor pressure. Thus, the work which a molecule does in evaporating from a liquid surface is $\phi = KT \ln P$, where ϕ is the work, K the Boltzmann constant, T the absolute temperature and P the relative vapor pressure. Also, the amount of work done in reversibly transferring one mole of vapor from the

interior of the free liquid to a point on the adsorption surface is $KT \ln P$, where again P is the relative vapor pressure. It seems that the difference in pressure influences only the rate of attainment of equilibrium at the saturation pressure.

Dewar⁸ found that in general, the gas with the highest boiling point was most strongly adsorbed, while Schmidt and Hinteler⁹ found apparently the reverse, that is, the adsorption on charcoal of a number of vapors at their

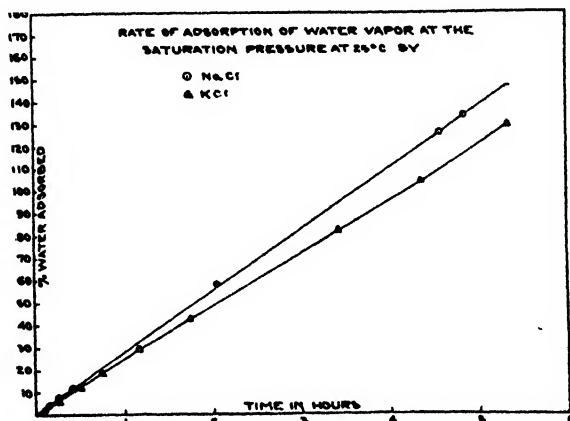


Fig. 9

saturation pressures was inversely proportional to the molecular volumes at the boiling point. However, the two general laws are applicable to entirely different portions of the adsorption isotherm and are not contradictory (see Pearce and Johnstone).¹⁰

Cellulose acetate (13.7% acetyl) adsorbed 12.3% benzyl alcohol at the saturation pressure.

Fig. 9 shows the rate of adsorption of water vapor by sodium chloride and by potassium chloride at the saturation pressure at 25° C. The rate curves are practically straight lines up to 130% adsorption. Before this point had been reached both salts had formed liquid solutions. These curves are introduced in order to show the type of rate curves to be expected in the adsorption of a solvent vapor by a solid. The adsorbed water is also rapidly removed from sodium chloride by evacuation at room temperature—only 0.7% remaining after 1 hour and none after 15 hours.

Fig. 10 shows the rate of adsorption of n-heptyl alcohol by a secondary cellulose acetate (37.25% acetyl) both in precipitated and in sheet form. The sheet adsorbs alcohol very slowly compared with the precipitated acetate. It is obvious that the exposed surface is an important factor. That the influence of molecular size of adsorbed vapor is also very great is seen when we consider that either precipitated or sheet cellulose acetate adsorbs water vapor at the same rate and to the same extent.

In general, we may conclude that the adsorption of non-solvent vapors is increasingly influenced by external surface, the greater the size of the vapor molecules.

It is practically certain that the rate of adsorption of all of the alcohols by precipitated acetates will vary depending on the state of aggregation.

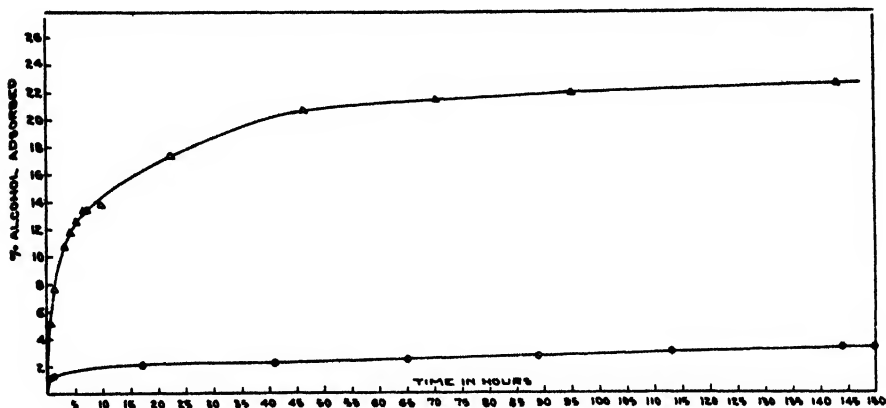


FIG. 10

Rate of adsorption of N-Heptyl Alcohol by Cellulose Acetate (37.25% Acetyl) in Precipitated and Sheet Form.

△ Precipitated

○ Sheet

TABLE II

Volume of Adsorption Space of Cellulose Acetate

Adsorbate	x/m	d	x/m/d
Water	0.165	0.998	0.165
Methyl alcohol	.256	.792	.323
Ethyl "	.381	.789	.483
n-Propyl "	.372	.804	.463
n-Butyl "	.294	.810	.363
n-Amyl "	.419	.817	.513
n-Hexyl "	.515	.820	.628
n-Heptyl "	.568	.817 (22°C.)	.696
n-Octyl "	.501	.827	.605

x/m = grams of vapor adsorbed per gram of acetate at the saturation pressure at 30°C.

d = density of liquid adsorbate at 20°C.

x/m/d = volume of adsorbed vapor.

Table II shows the volumes of the different alcohols adsorbed by a given secondary cellulose acetate (38% acetyl). The volume is not constant. Coolidge¹¹ found that the volume of a number of vapors adsorbed on charcoal at the saturation pressure at 0°C. varied only from 0.424 to 0.494 cc. per gram of charcoal, and he suggested that the adsorbent presents a fixed volume rather than a fixed surface. But cellulose materials being elastic gels, show neither a fixed volume nor a fixed surface.

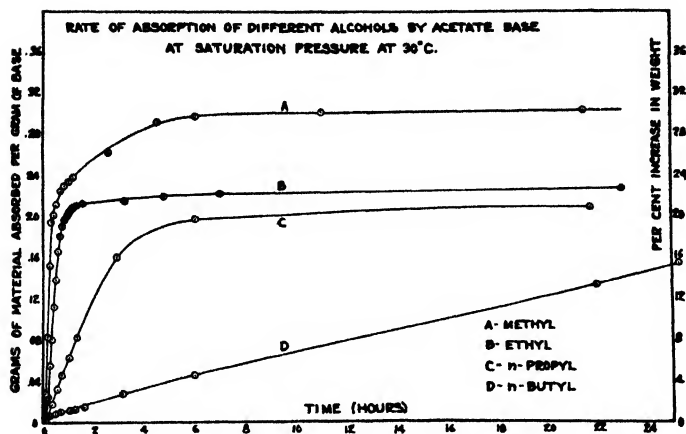


FIG. 11

Adsorption and Desorption of Alcohol Vapors by Cellulose Acetate Sheet

Whereas all of the data presented so far in this paper were obtained with samples of precipitated or fibrous material, the following measurements were made on a sample of cellulose acetate sheet, 0.003" thick, prepared from a secondary cellulose acetate (38% acetyl) and acetone. The sheet was heated 24 hours at 105°C. to remove the acetone.

The difference in the rate of sorption of the different alcohols is much more pronounced in the sheet than in the precipitated form (see Fig. 11). The rate of adsorption as well as the maximum adsorption decreases regularly in going from methyl to n-butyl alcohol.

Fig. 12 shows the rate of desorption of the different alcohols by evacuation at 30°C. As the higher alcohols were more slowly adsorbed by the sheet, so

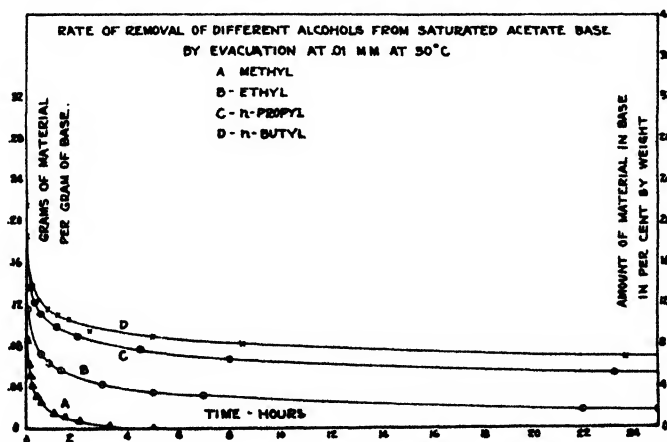


FIG. 12

they are more slowly removed from it independently of the total amount adsorbed at saturation. This behavior is to be expected because of the lower vapor pressure and greater molecular size of the higher alcohols with the consequent lowering of the diffusion rate. It should again be noted that all of the water adsorbed by a piece of sheet can be completely removed by the above evacuation procedure in about 30 minutes, whereas the lowest alcohol requires 5 hours.

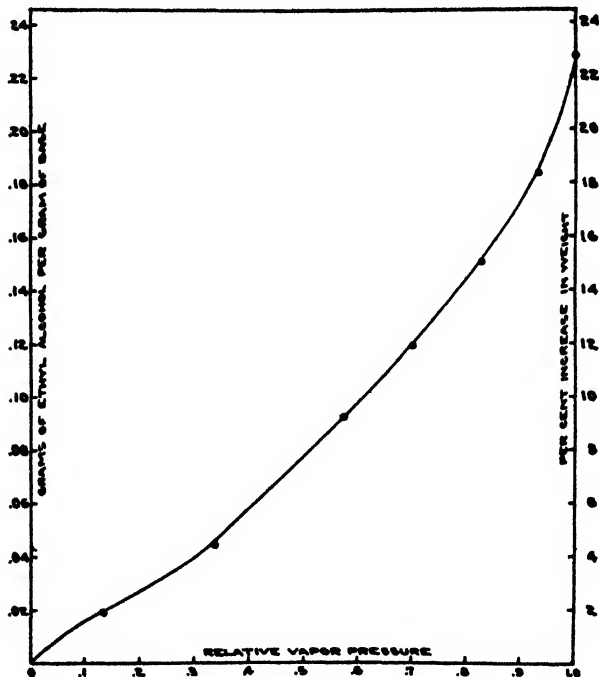


FIG. 13

Sorption of Ethyl Alcohol by Acetate Base at 30°C

Fig. 13 shows the maximum adsorption of ethyl alcohol vapor at different relative vapor pressures at 30°C. by a sample of the same sheet as used above. We have a typical S-shaped isotherm similar in all respects to the moisture adsorption isotherm. A calculation of the pore radius using the Kelvin equation gives the distribution curve shown in Fig. 14 with a most probable pore radius of 4.4 Å.U. in fair agreement with the value of 5.5 Å.U. obtained from the moisture adsorption isotherm.

Some information may be gained from a comparison of the alcohol and water adsorption data. Alcohol adsorption by cellulose and cellulose acetates is much more profoundly affected by chemical composition and mechanical structure than water adsorption and hence may yield more conclusive evidence regarding the mechanism of adsorption by such materials. The fact that water is adsorbed just as rapidly and to the same extent by a cellulose acetate in either sheet or precipitated form and that all of the water adsorbed at the saturation pressure may be removed by evacuation at room temperature

within 10 minutes indicates that the mechanical structure offers no impediment to the diffusion of water molecules in such a material. Neither is there any indication here of pronounced chemical attraction between cellulose acetate and water although, since the moisture adsorption does vary with acetyl content, specific chemical forces must play a part. On the other hand, even the smallest alcohol molecule has difficulty diffusing in and out of the cellulose acetate material. Specific chemical or polar forces are insufficient to attract strongly any of the alcohols, yet a large molecule of a solvent vapor

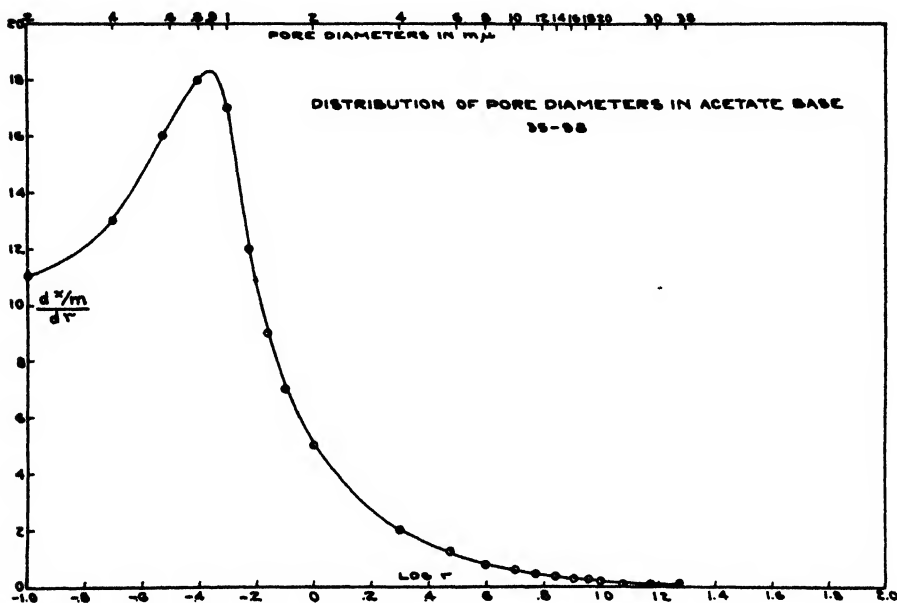


FIG. 14

is strongly attracted and adsorbed. The attractive force overcomes the resistance to diffusion and the material swells and finally dissolves in the adsorbate. On desorption the last traces of this vapor are removed more slowly than adsorbed alcohols because of the stronger attraction between adsorbent and adsorbate and also increasing resistance to diffusion due to collapse of pore space.

Summary

The rates of adsorption of the normal saturated alcohols up to n-octyl by cellulose and a series of primary and secondary cellulose acetates were determined at the saturation pressures at 30°C. The rates of adsorption and desorption of methyl, ethyl, n-propyl and n-butyl alcohols by a certain cellulose acetate sheet were determined at 30°C. as well as a complete isotherm of the adsorption of ethyl alcohol by the same material at 30°C.

Alcohol adsorption by primary acetates increases with increasing acetyl content and n-propyl and n-butyl alcohols give maxima at 32% acetyl.

Secondary acetates show greater adsorbing power than primary acetates. In general, higher alcohols are found to be adsorbed and desorbed more slowly than the lower alcohols. Also, higher alcohols are adsorbed more slowly by cellulose acetate in sheet form than in precipitated form. It is found that the adsorption of different alcohols expressed in moles per gram of cellulose material decreases rapidly with increasing number of carbon atoms and becomes approximately constant at n-butyl.

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*Rochester, N. Y.,
May 14, 1932.*

THE STRUCTURE OF GELATIN SOLS AND GELS

Part IV. Fluidity and Hydrolysis*

BY S. E. SHEPPARD AND R. C. HOUCK

In a previous paper¹ there was presented an extended study of the effect of temperature change on the fluidity of gelatin sols. Using a de-ashed gelatin, fluidity-time curves at different pH values were obtained at 40°C., 50°C., 60°C., 70°C., and 85°C. Initially the curves sufficiently approached straight lines for their slopes to be taken as measures of the rate of change of fluidity. The slope, $\Delta\phi/\Delta t$, plotted as function of pH, gave at each temperature a curve showing a flat minimum. These curves sufficiently resembled the logarithmic form of the catalytic catenary² of Hudson to allow the conclusion that ϕ_k , the fluidity change constant, was proportional to $\log K$, where K was the actual velocity constant of hydrolysis.³ On the other hand, if ϕ_k is considered as proportional to the actual velocity constant of hydrolysis, then it is found that the comparison of the family of $\log \phi_k \sim \text{pH}$ curves with Northrop's $\log K \sim \text{pH}$ curves is somewhat closer. Fig. 1 shows the actual curves. Plotting the data in this manner indicates more clearly that the slopes of the straight line on the acid side and on the alkaline side of the flat portion of the $\log \phi_k \sim \text{pH}$ curve are practically the same for all the temperatures employed. Further, it appears to be probably the better method of plotting since by considering ϕ_k the velocity constant, the usual methods employed in chemical kinetics for studying a reaction can be employed.

Further evidence, pointing to hydrolysis of gelatin molecules as the main cause of the decrease in viscosity with time, has been found by calculating the heat of hydrolysis from the ϕ_k values at constant pH and at different temperatures.

The heat of hydrolysis is calculated by application of the van't Hoff expression dealing with the relation of the velocity constant and temperature. This expression is as follows:

$$\frac{d \log k}{dT} = \frac{Q}{RT^2}$$

in which k = velocity constant

T = absolute temperature

Q = heat of reaction

R = gas constant expressed in calories

A study of this relation indicates that a linear relation should exist between the logarithm of the velocity constant and the reciprocal of the absolute temperature.

*Communication No. 493 from the Kodak Research Laboratories.

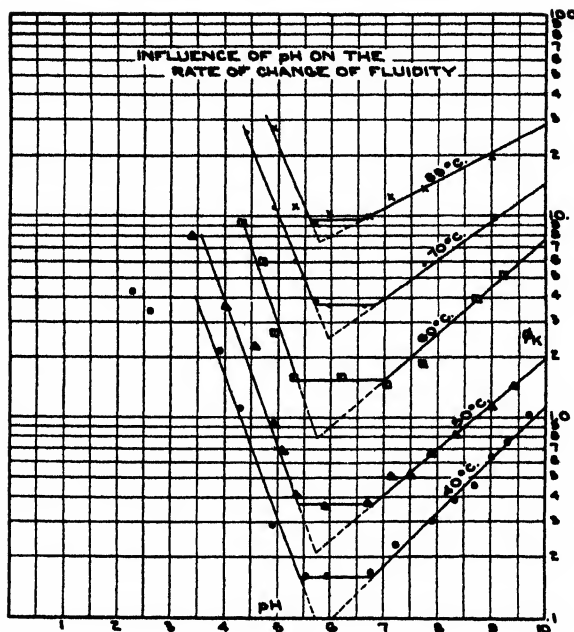


FIG. 1

Accordingly, $\log \phi_k$ values at the same pH, but different temperatures, were plotted against the reciprocals of the absolute temperatures. The results obtained are shown by Figs. 2 to 3. With pH's up to 5.4, fairly good straight lines were obtained, provided the results at 85°C. were excluded. The ϕ_k values at this high temperature appear to be too low, possibly due to a change in the reaction products. A very satisfactory straight line was obtained over the pH range 5.6 – 6.8, in which the velocity constant is practically independent of pH at all temperatures studied. At pH 8.0 and above, straight lines were not obtained, indicating that probably there are other disturbing factors in this region as well as hydrolysis.

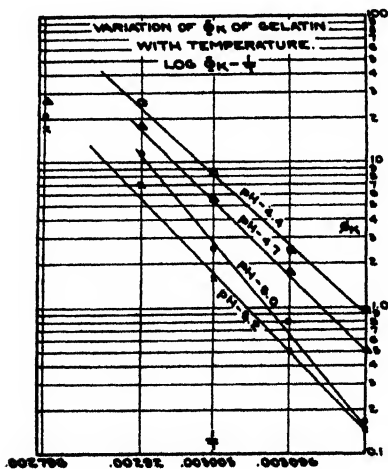


FIG. 2

Inspection of the van't Hoff equation, particularly in the integrated form:

$$\log_{10} \frac{K_2}{K_1} = \frac{Q}{2.303 R} \frac{T_2 - T_1}{T_2 T_1}$$

shows that the heat of the reaction is obtained by multiplying the slope of the $\log \phi_k \sim 1/T$ curve by $2.303 R$, where R is the gas constant expressed in calories and is equal to 1.98. This was done for those cases where the $\log \phi_k \sim 1/T$ graph was a straight line. The results obtained are shown by Table I.

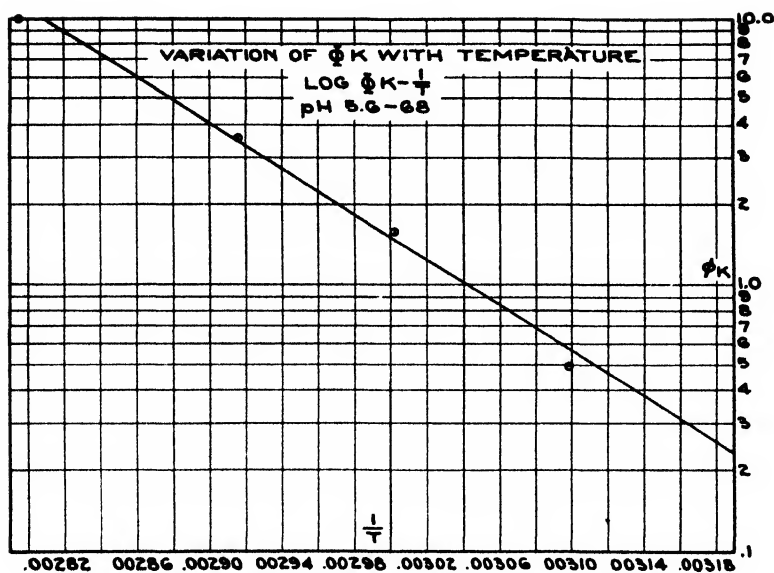


FIG. 3

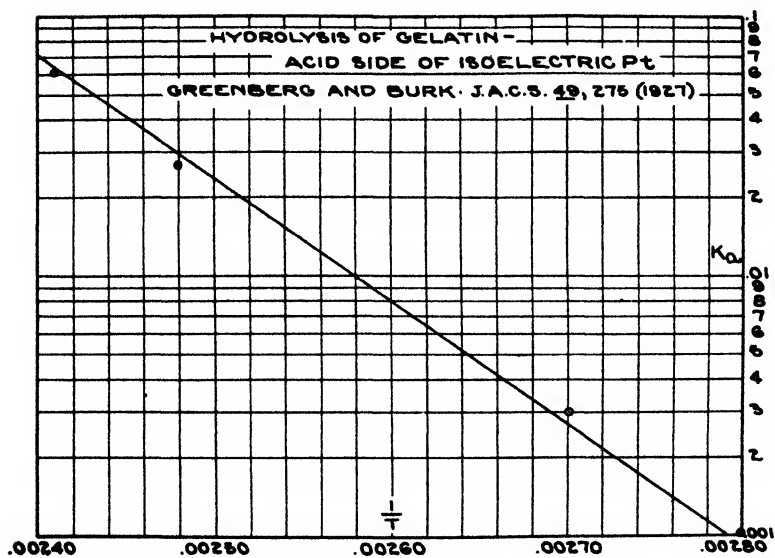


FIG. 4

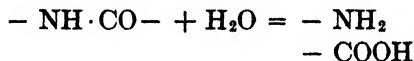
TABLE I
Heats of Hydrolysis of Gelatin No. 36

pH	Slope	Heat of Hydrolysis of Gelatin (calories)
4.4	5258	24,000
4.7	5522	25,200
5.2	5825	26,540
5.6 — 6.8	4735	19,920
		(Mean 23,915 cal.)

These values appear to be significant when comparison is made with the value for the heat of hydrolysis of gelatin calculated from velocity constants determined chemically. Greenberg and Burk⁴ determined the velocity of hydrolysis of gelatin at high temperatures by autoclaving and measuring the amino-acid content by the Van Slyke method. They calculated a constant K_a , involving the activity coefficient. By plotting $\log K_a$ against $1/T$, a fair straight line is obtained, as shown by Fig. 4. The authors preferred to plot $\log K_a$ against T . Calculation of the heat of hydrolysis in the usual manner from the slope of the $\log K_a \sim 1/T$ curve gives a value of 21,480 calories.

A comparison of this value of 21,480 calories with the values obtained from fluidity changes and shown in Table I indicate them to be of the same order of magnitude. It is believed that this agreement is further proof that the fluidity changes are mainly due to hydrolysis of molecules.

The hydrolysis in this case may be most simply represented as a splitting of peptide linkages.



It is known that this reaction does not proceed to complete hydrolysis (with formation of free amino-acids) save in very strongly acid solutions at temperatures of the order of 100°C. In strongly alkaline solution the hydrolysis is accompanied by racemization.⁵ It may be considered probable, therefore, that above a certain temperature the end product of the reaction is different—and hence the final fluidity value. Since the initial slope $\Delta\phi/\Delta t$ depends both on the final state of the system, as well as on the reaction velocity, this may explain the discrepancy for the 85°C. value.

The high viscosity of gelatin sols—as of other solutions of “high molecular” bodies—has been frequently attributed to solvation, whereby it is assumed that the molecules or micelles are surrounded by a solvate sheath of solvent molecules of which the inner layers are held with stronger, the outer with weaker forces.⁶ These solvate molecules would be under considerable compression, so that if the fluidity change on heating gelatin sols consisted in increase of free water molecules, or breakdown of solvate sheaths, one would expect a definite increase in specific volume. We have studied, therefore, the dilatometry of gelatin sols at the same time as the viscosimetry. The method employed was somewhat similar to that used by The Svedberg⁷ and by Neville

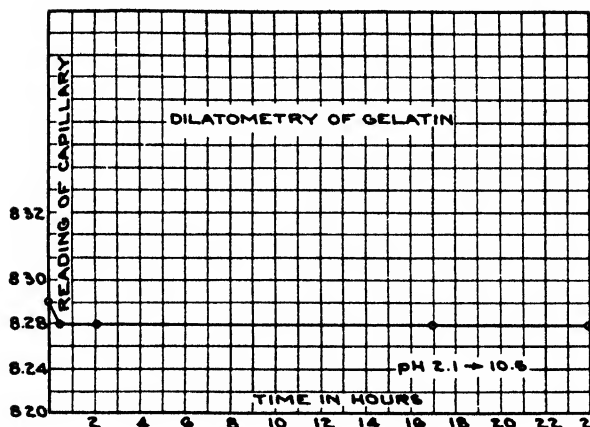


FIG. 5

and Jones.⁸ A gelatin sol was prepared at the desired pH, and placed in the bulb of the dilatometer. The capillary was sealed on, and after evacuation the remainder of the bulb and capillary were filled. This method was adopted to avoid any uncertainty as to possible leaks around a ground-glass joint or stop-cock. Volume changes were followed with a cathetometer.

The results at 50°C. for solutions between pH 2.1 and pH 10.5 are shown in Fig. 5. Over this range there is no change in volume during a period of 24 hours, while the fluidity has increased very considerably. After this time there usually followed a slight decrease (contraction). On the other hand, a sol of pH 12.0 showed a very noticeable increase in volume (Fig. 6). The fact that more far reaching changes occur in strongly alkaline solutions has already been noted. But the constancy of volume over the pH range 2 — 10, when the fluidity is steadily increasing, appears to exclude the explanation of the viscosity of protein sols in terms of solvate sheaths. Together with the shape of the pH ~ velocity curves, the temperature coefficient, and the calculated heat

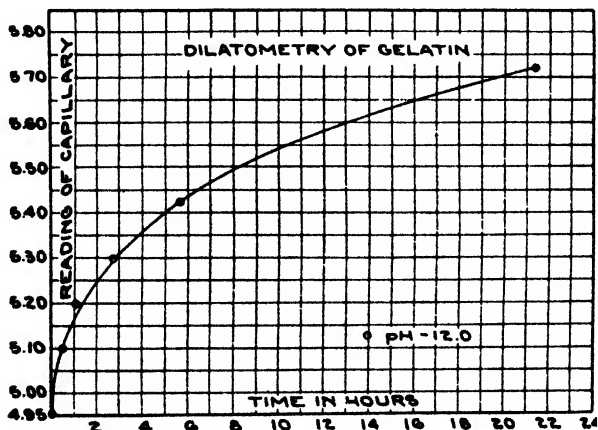


FIG. 6

of reaction, this points to the conclusion that the viscosity is due to the presence of large molecules (macromolecules in Staudinger's sense) and decreases with hydrolytic fission of these macromolecules. If there is any true solvation of these molecules, it must consist in a monomolecular layer of oriented water dipoles, the amount of which is not substantially altered by transection of the macromolecules. As pointed out in the second paper of this series, these appear to be relatively elongated, thin structures, in accordance with (a) spreading experiments giving a thickness of 7 Å.U., and (b) anisotropy of stretched and dried gelatin gels.

Summary

1. $\log \phi_k \sim 1/T$ curves were plotted for gelatin and fair straight line fits obtained. From the slopes of these lines heats of hydrolysis were calculated which varied from 19,900 to 26,500 calories, depending on the pH.
2. The heat of hydrolysis of gelatin obtained by calculation using the data of Greenberg and Burk was found to be 21,480 calories.
3. The general agreement, at least so far as order of magnitude is concerned, of our values with that of Greenberg and Burk, is considered further evidence that the fluidity changes are mainly due to hydrolysis of large molecules, rather than to disgregation of micelles.
4. Dilatometric experiments, establishing constancy of specific volume during hydrolysis and fluidity increase, show that the high viscosity of gelatin sols is not due to solvation.

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Rochester, N.Y.,
May 14, 1932.

THE DECOMPOSITION OF ETHYL BROMIDE, ALKYL HALIDES, AND ACETAL IN THE GAS PHASE AT 300°-400°*

BY EDWARD T. LESSIG¹

The object of this investigation was to find new unimolecular reactions with which to test theories of kinetics. To be of value in the study of kinetics, a reaction should proceed according to a simple stoichiometrical equation and it must be uninfluenced by the walls of the containing vessel. Of the thirteen compounds investigated here, the thermal decomposition of ethyl bromide into ethylene and hydrobromic acid is particularly significant; but the decomposition of propyl bromide, acetal and isobutyl chlorocarbonate are also interesting. Some of the other decompositions are worthless in the study of kinetics but they are described briefly as empirical facts. The data are to be regarded only as semi-quantitative, and suggestive of further investigations in kinetics.

Apparatus and Procedure

The decomposition of the organic vapors was followed by pressure measurements, using the all-glass apparatus and diaphragm² developed in this laboratory. The reaction chamber, made from a 250 cc flask of pyrex or quartz, and the thermostat are shown in Fig. 1. It was deemed essential in this work to keep every part of the reaction chamber up to the full temperature of the thermostat. In this way there was no opportunity for the vapor to condense in a tube leading to a manometer at room temperature. The pressure in the reaction chamber was balanced through a sensitive glass diaphragm against a measured air pressure. The point of balance was determined by electrical contact through platinum wires one of which was attached to the diaphragm. When quartz reaction chambers were used the technique was similar except that the platinum wires, used for the contacts, were anchored mechanically by melting into small capillaries of quartz which were then sealed into the diaphragm and into the chamber. It was necessary also, to hold the side wire tight with a spring. Otherwise the difference in thermal expansion caused the wire to sag away from the contact at the higher temperatures. Sparking with an induction coil usually served to rejuvenate the contacts when they became fouled. A loose packing of glass wool kept the wires separate and prevented circulation of cold air down to the diaphragm.

* Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin.

¹ This communication is based on a thesis submitted for the Ph.D. degree at the University of Wisconsin in 1929. The investigation was carried out under the direction of Farrington Daniels.

² Daniels: J. Am. Chem. Soc., 50, 1115 (1928).

The thermostat consisted of a rectangular iron box $30 \times 20 \times 20$ cms filled with molten lead and well insulated with transite and 12 cms of loose asbestos. Heating units of nichrome wire on transite board were placed around the box. The lead was stirred with an iron stirrer driven by a motor. The temperature was determined with a Leeds and Northrup platinum resistance thermometer and precision bridge. The heating units in two separate circuits were controlled by hand. When the line voltage varied as indicated by a meter in the circuit, the necessary compensation was made by adjusting

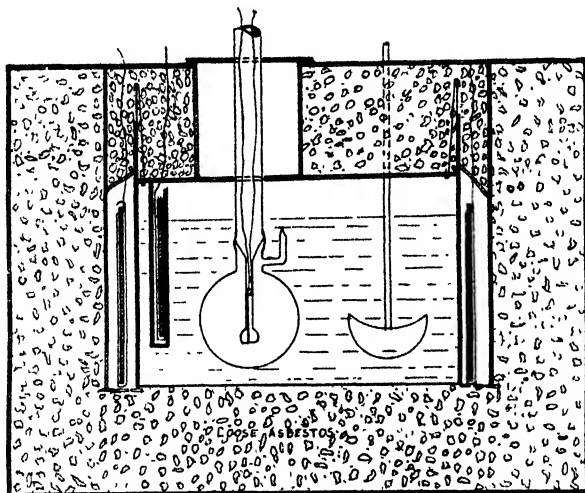


FIG. 1
Reaction vessel and thermostat

a reactance coil in series with the heating units. In this way it was possible to keep the temperature constant within 0.2° .

If the decomposition products (ethylene in the case of ethyl bromide) remained long in the reaction chamber a film of carbon was deposited on the walls. Such a film, if allowed to remain, gave erratic results in any subsequent experiments. Accordingly the chamber was cleaned each time with chromic acid, rinsed and dried; and then filled with oxygen and heated to redness.

In carrying out an experiment the zero point is first determined with the flask fully immersed in the thermostat and the side arm of the reaction chamber extending out to the air. The flask is then raised slightly and the side arm is drawn down to a capillary. A small glass bulb about 1 cm in diameter is made with a capillary tip. The bulb is filled with the liquid to be used, and sealed off while the liquid is boiling under reduced pressure. In this way air is excluded. After making a file scratch, the capillary is inserted through a stout rubber tube into the capillary of the side arm. The connections with the rubber tube are made still tighter with deKhotinsky cement. The whole flask is then evacuated with an oil pump through a tube fused onto the side arm. When all the air has been removed the line to the

pump is fused off, the bulb is moved sideways so as to break the capillary and the liquid vaporizes to fill the reaction chamber. Since the capillary of the bulb extends well beyond the connection, the vapor does not come in contact with any rubber. No stopcocks are used.

The side arm of the flask is then sealed off and the flask is immediately lowered into the thermostat bath as shown in Fig. 1. Pressure readings are taken at frequent intervals by observing the outside pressure which is just necessary to permit contact of the platinum points. Typical pressure-time curves are given later.

The pressure-time data are used in different ways to calculate the specific reaction rates and to test for unimolecularity. When the pressure does not change any more the decomposition is assumed to be complete, and the difference between this final pressure P_f and the pressure at any time P_t , in the simplest cases, is a measure of the amount of undecomposed material. The initial pressure P_i may be obtained by extrapolating the curve to zero time. The accuracy of this extrapolation varies with the steepness of the slope. If one molecule decomposes into two the final pressure should be twice the initial pressure except for a recombination of the products. If three molecules are produced on decomposition, the final pressure should be three times the initial. If the reverse reaction is appreciable, however, an equilibrium will ensue and the final pressure will be less than the expected pressure. The simplest way of testing for unimolecularity is to determine the period of half and three-quarter life. If the reaction is of the first order and the reverse reaction is negligible the time taken for the value of $P_f - P_t / P_f - P_i$ to become $3/4$ will be twice as great as the time for it to become $1/2$. The value of the specific reaction rate k is $0.639/t_{1/2}$ where $t_{1/2}$ is the period of half life.

When the data justify it, they are treated more completely by plotting $\log (P_f - P_t)$ against the time t . The straightness of the line indicates the extent to which the reaction follows the first order equation and the slope of the line multiplied by 2.303 gives the value of the specific reaction rate, k .

These methods do not allow for the reverse reaction and can not be considered exact unless the final pressure is exactly twice (or three times etc.) as great as the initial pressure. A more accurate method was used in some of the experiments on ethyl bromide where the reverse reaction is bimolecular. Representing the initial concentration of ethyl bromide by a , the amount decomposed by x , and the equilibrium constant K by the ratio k/k' where k is the velocity constant of the dissociation reaction and k' is the velocity of the recombination reaction,

$$dx/dt = k(a-x) - k'x^2 = k [(a-x) - (x/K^2)]. \quad (1)$$

The integrated form was used as follows,

$$k = \frac{1}{t} \frac{2.303}{\sqrt{4a/K+1}} \log \frac{(+2x/K+1+\sqrt{4a/K+1})(-1+\sqrt{4a/K+1})}{(-2x/K-1+\sqrt{4a/K+1})(+1+\sqrt{4a/K+1})} \quad (2)$$

Ethyl Bromide

The first 22 experiments were carried out with an impure preparation, synthesized in a student laboratory. In general there was an inflection in the early part of the pressure curve indicating some complication. Experiments with air alone under similar conditions showed that equilibrium was reached within five minutes. The large inflections noted can not be attributed to thermal lag alone.

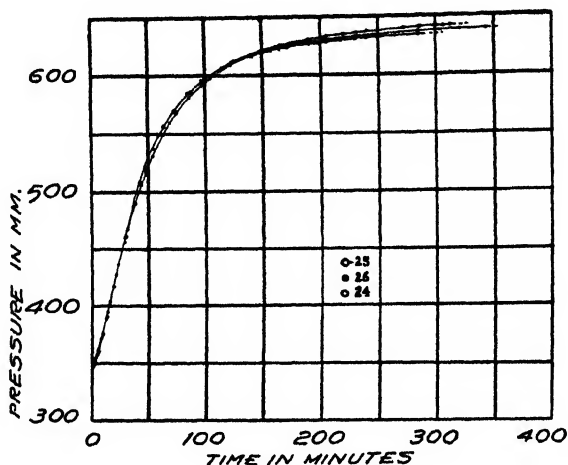


FIG. 2
Dissociation of Ethyl Bromide

Experiments 23-32 were made with preparation B, a high grade product from the Eastman Kodak Company which was further distilled several times. Fig. 2 is typical of this group. Three check experiments, at nearly the same initial pressures, are seen to agree closely.

In the last and most significant experiments, 33-48, preparation C was used. This was very pure material prepared in the laboratory of Professor Timmermans at Brussels under the auspices of the International Union of Pure and Applied Chemistry and distributed through the U. S. Bureau of Standards.¹ Figs. 3 and 4 give some of these results in detail. It will be noted that the inflections have nearly disappeared in these cases.

The final pressure was always a little less than twice the initial pressure. The reaction follows the equation



but the reverse reaction becomes appreciable particularly at the end of the experiment. In some cases the products of the reaction remaining at the end of an experiment were analyzed, chemically. The flask was cooled and the

¹ Several liquids are now available in small quantities. They are guaranteed to have the constants described by Timmermans and Martin in *J. Chim. phys.*, 23, 733 (1926) and later communications. Investigators greatly appreciate this convenient means for getting samples of pure organic liquids.

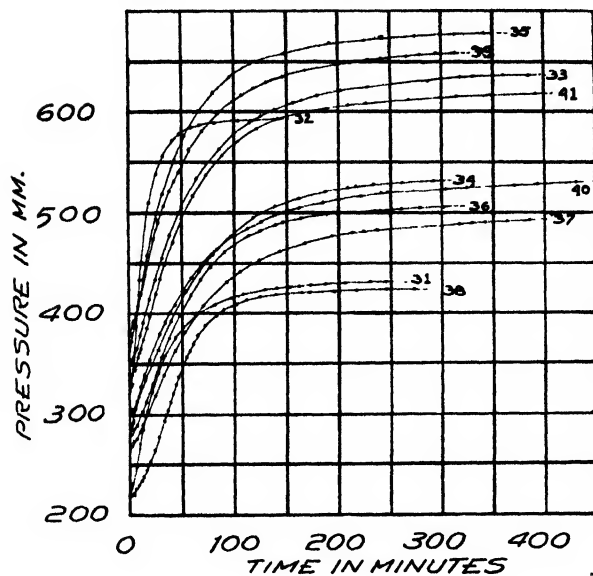


FIG. 3
Dissociation of Ethyl Bromide

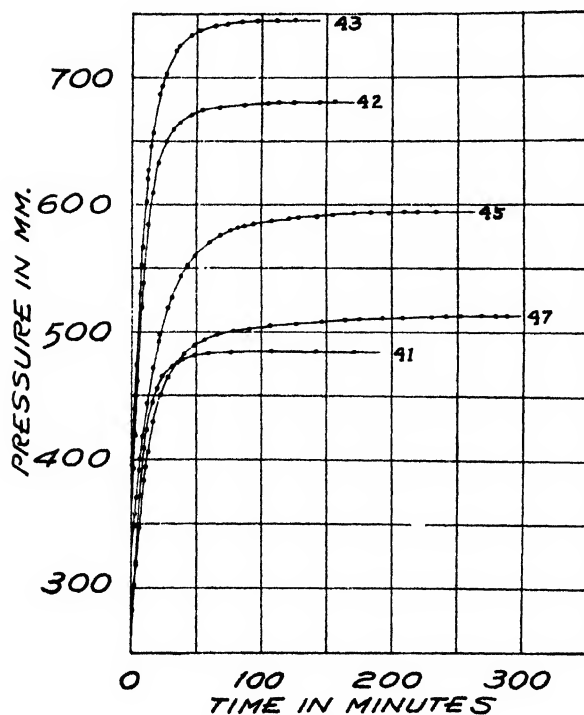


FIG. 4
Dissociation of Ethyl Bromide

tip broken off under air-free water. No free bromine was found in the solution as tested with starch-iodide solution. The reaction flask was never colored red, even when withdrawn quickly from the thermostat and it may be concluded that bromine is not formed under the conditions of these experiments. Even if hydrobromic acid did dissociate in the thermostat into bromine and hydrogen the pressure measurements would not be affected because such a dissociation involves no volume change.

The gas remaining after the absorption of hydrobromic acid in the water was found to be ethylene. It was completely absorbed in bromine water, a

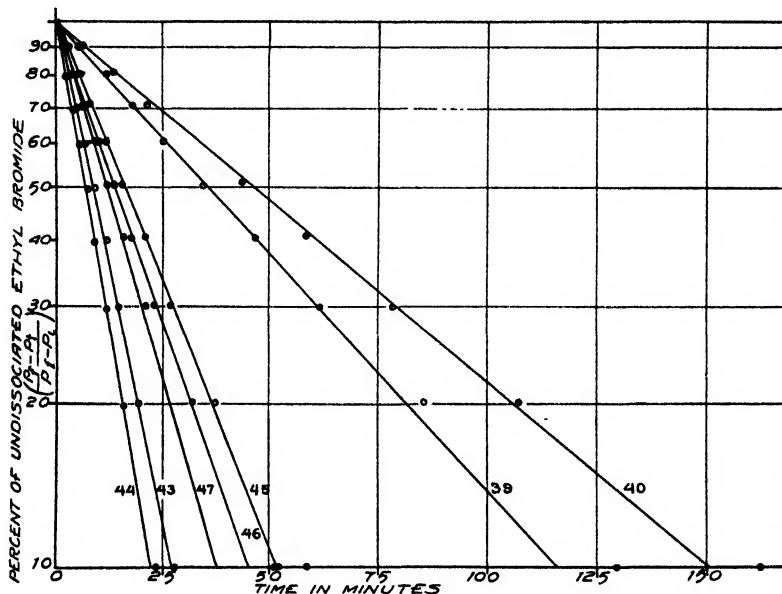


FIG. 5
Dissociation of Ethyl Bromide

fact which indicated that it was composed of unsaturated hydrocarbons and that neither hydrogen nor saturated hydrocarbons were present. After explosion with oxygen the shrinkage due to water formation was 10.0 cc and the shrinkage due to absorption of the remaining carbon dioxide in sodium hydroxide solution was practically the same—9.8 cc. After removal of the hydrobromic acid in water, then, the gas must have contained twice as many hydrogen atoms as carbon atoms. Furthermore, a small amount of liquid ethyl bromide was sealed off in a small bulb in the absence of air and weighed. The bulb was broken in an evacuated flask of known volume and the observed pressure agreed with the pressure calculated from the simple gas laws, both before and after decomposition.

The fact that this dissociation is essentially first order is shown by the straight lines of Fig. 5 in which $\log (P_t - P_\infty)/(P_i - P_\infty)$ is plotted against time for a few typical experiments. In plotting these graphs the values of $P_i - P_\infty$

TABLE I
The Dissociation of Ethyl Bromide

Expt. No.	Temp. °C.	Material	Initial Press. mm.	$k_1(\text{min}^{-1})$ Slope	$k_2(\text{min}^{-1})$ Statist.	$k_3(\text{min}^{-1})$ Corr.	$k_4(\text{min}^{-1})$ Elim.
16	356.4	A		-0.031	0.0284	0.038	
17	358.5	A	343	.035	.0329	.043	
22	356.5	(A)	335	.013			
23	358.0	(A)	340	.005			
24	375.0	B	345	.019	.0194		
25	374.5	B	347	.022	.0212		
26	374.5	B	345	.021			
27	373.0	B	463	.027	.0281		
29	373.0	B	508	.029	.0288		
31	387.5	B	215	.034	.0303		
33	372.5	B	350	.017			
34	371.0	C	295	.016		.011	.010
35	369.3	C	277	.022	.0219		
36	369.5	C	277	.019		.011	.011
37	370.0	C	265	.016		.011	.010
38	375.5	C		.029	.0221		
39	375.5	C	358	.019	.0198	.017	.017
40	375.5	C	282	.015		.016	.016
41	401.7	C	263	.098		.072	.072
42	401.7	C	366	.095		.075	.064
43	401.7	C	390	.089		.070	.064
44	401.7	C	647	.107		.065	.064
45	388.0	C	331	.044		.033	.033
46	388.0	C	600	.056		.034	.034
47	388.0	C	281	.066		.040	.038
48	388.0	C	331			.038	.037

No. 22 Material A purified.

No. 23 Material A twice purified.

Nos. 41-48 and No. 31-32 in quartz vessel. All others in pyrex.

No. 17 Excess of glass surface.

were taken from the smooth pressure-time curves at intervals corresponding to 10, 20, 30 etc. per cent decomposition.

The experimental determinations on ethyl bromide are summarized in Table I. The specific reaction rates calculated from the slopes of the logarithmic graphs are given under k_1 . The values of the rate-constants as calculated from the same data using a statistical method are given under k_2 . The rate constants corrected for the reverse reaction by using equation (2) are given under k_3 . In these calculations the equilibrium constant K was estimated from the difference between the final pressure and twice the

initial pressure. In the calculation of k_4 the reverse reaction is practically eliminated by measuring the time required for the pressure to increase to $1\frac{1}{4}$ times its original value. This time is then divided into 0.289 (i.e. $2.303 \log 1\frac{1}{4}$). It will be noted that whereas k_1 and k_2 increase with pressure, k_3 and k_4 are nearly independent of pressure over the range studied here. k_3 and k_4 are more nearly correct than k_1 and k_2 .

Only a few of the data on the impure material are given here. It is sufficient to state that this material decomposed much more rapidly than the pure material; that an induction period was often present at the beginning during which there was little decomposition; and that the constant k appeared to be distinctly larger at high pressures. The logarithmic graphs were less satisfactory than those shown in Fig. 5, and they often intersected the ordinate above 100 per cent. The influence of impurities on the reaction rate is shown by a comparison of experiments 17, 22 and 23—the refractive indices of which were respectively 1.4255, 1.4248 and 1.4240.

It was found that increasing the surface of glass five fold by inserting additional pieces caused no change in the decomposition rate. This fact combined with the large temperature coefficient showed that the decomposition is not a wall reaction. In two other experiments it was found that the addition of an excess of bromine caused a considerable increase in the rate of decomposition.

It will be noted that there is no marked difference in decomposition rate between the experiments in pyrex and those in quartz,—another fact which indicates that the reaction is not a wall-reaction.

When $\log k_4$ is plotted against $1/T$ the best straight line through the somewhat scattered points leads to a value in the neighborhood of 50,000 calories for the energy of activation of ethyl bromide.

The study of ethyl bromide has been continued in this laboratory, particularly at low pressures, and additional material will be published shortly.

Propyl Bromide

Normal and isopropyl bromide were obtained from Professor Timmermans' laboratory. The results¹ were less satisfactory than those for ethyl bromide. The data on normal-propyl bromide are summarized in Table II.

It is evident from this table that the reaction is first order, but that there is a reverse reaction which prevents the final pressure from becoming twice as great as the initial pressure. The decrease in the constant with a decrease in pressure is striking. This phenomenon may be accepted as a qualitative fact but the quantitative interpretation must await further, more accurate experiments. As in the case of ethyl bromide *part* of this decrease is due to the reverse reaction which has not been allowed for in the calculations of Table II. The experiments with extra glass surface, having a five-fold increase, indicate that the decomposition is not a wall reaction. Two isolated experiments suggest that a trace of propyl alcohol retards the decomposition whereas a

¹ The physical constants are given in *J. Chim. phys.*, **23**, 733 (1926); **25**, 15 (1928).

TABLE II

Rate of Dissociation of n-Propyl Bromide

Temp. °C.	Initial Pressure	Final Pressure	Period of—		k	Remarks
			½ life	¾ life		
353.5	274 mm	504 mm	12 min	26 min	0.058 min ⁻¹	
	237	451	13	29	.053	
	215	397	11	24	.063	
	168	316	12	27	.058	
	164	—	15	33	.046	
	150	—	17	38	.041	
	127	250	17	41	.041	Glass × 5
	119	222	12	25	.058	Glass × 5
	92	128	17	34	.041	
	54	106	26	52	.027	
364	301	537	8	18	.087	
	250	450	8	17	.087	Saturated with H ₂ O
	217	396	9	21	.077	
	201	388	14	24	.050	Trace n-C ₃ H ₅ OH
	168	319	9	21	.077	Trace Bromine
	165	323	10	20	.069	
	131	243	11	23	.063	
	100	188	12	26	.058	
	95	180	5	11	.14	10 mm. n-C ₃ H ₅ OH
	73	136	16	32	.043	
	61	118	15	29	.046	
	14	27	20	40	.035	
374	274	473	6.5		.11	
	168	309	6		.115	
	94	182	7.0		.10	
	77	146	7.0		.10	

larger amount accelerates it. It has been established that oxygen greatly accelerates the rate at which the pressure rises and some of the abnormal results may be explained by the presence of a little air. A small amount of water vapor had practically no influence on the decomposition.

The propyl alcohol itself decomposed slowly in an erratic manner. The addition of methyl propionate and propyl acetate did not cause any large change in the rate of decomposition of propyl bromide.

The data on iso-propyl bromide were still less satisfactory. All the decompositions were first order as shown by the fact that the period of three-quarter life was roughly twice the period of half life. However, six independent determinations at 346.5°C. ranging from 116 to 213 mms initial pressure gave constants which ranged from 0.05 to 0.17. Two determinations at 356.5 gave 0.10 and 0.17.

It has been established¹ before that *n*-propyl bromide decomposes on heating into propylene and hydrobromic acid. This fact was subjected to further test. No free bromine was obtained in the decomposition. After removal of hydrogen bromide the residual gas was completely absorbed in bromine water. Combustion of the gas indicated the formula C_3H_6 .

The situation is further complicated by the conversion of one isomer into the other. Michael and Leupold² found that at 262°C . 30.9 per cent of *n*-propyl bromide is converted into iso-propyl bromide in one hour and starting with pure iso-propyl bromide 1.8 per cent passes into the normal form in one hour.

The iso-bromide decomposes more easily than the normal and the normal may change over in part to the iso form before decomposing.

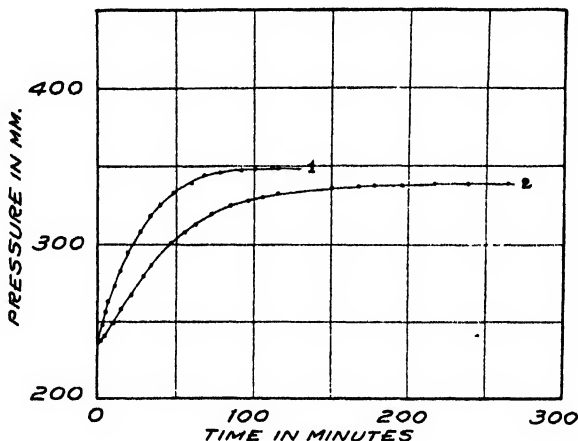


FIG. 6
Decomposition of Ethyl Iodide

Ethyl Iodide

Two isolated determinations were made on ethyl iodide from two different sources as shown in Fig. 6. In the first determination at 355° the initial pressure was 232 and the final pressure 350 mm giving a half life of 18.5 and a three-quarter life of 36 minutes. In the second determination at 345° $P_i = 235$ mm, $P_f = 340$, $t_{1/2} = 35$ mm and $t_{3/4} = 63.5$. The constants k , estimated from $t_{1/2}$, are respectively, 0.020 and 0.037. Although a graph of $\log(P_f - P_t)$ gives a very satisfactory straight line when plotted against time the reaction is complicated by the fact that the pressure did not double and by the fact that some free iodine was produced.

Alkyl Chlorides

The alkyl chlorides studied did not give straight lines when $\log(P_f - P_t)$ was plotted against time, although in some cases the pressure-time curves appeared to be smooth and normal as in Fig. 7. They are not simple first-order

¹ Brunel: Ann., 384, 245 (1911); Nef; 354, 327 (1907).

² Michael and Leupold; Ann., 384, 245 (1911).

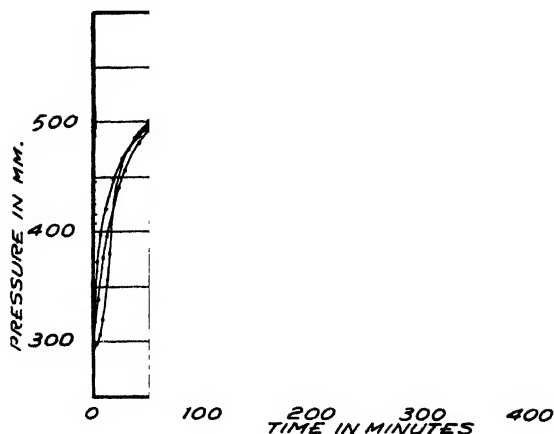


FIG. 7
Decomposition of tertiary Butyl Chloride

reactions. The empirical facts are summarized in Table III. The chloroform curve was very irregular. A yellow crystalline material together with a tar was produced.

TABLE III
Rate of Decomposition of Alkyl Chlorides

Compound	Temp.	P _i	P _f	Approx. ½ life
Ethylene Chloride	360°	355 mm	716 mm	(69) min.
Ethylene Bromide	328	175	355	(10)
Isopropyl Chloride	335	265	532	(85)
Tert-butyl Chloride	280	300	538	(17)
	300	294	542	(10)
	315	289	548	(18)
	350	Too fast to measure		
Ethylene Chlorohydrin	368	158	474	(141)
Chloroform	368	300	420	
	396	210	420	
	400	330	570	

Acetal and Methylal

Three experiments with acetal in pyrex vessels are summarized in Table IV.

TABLE IV
Decomposition of Acetal

Exp.	t°C.	P _i	P _f	t _½	t _¼	k
1	370°	173	518	21 min	43 min	0.033 min ⁻¹
2	360	227	680	34.5	68	.020
3	350	344	989	58	—	.012

The final pressure is nearly three times the initial pressure, a fact which indicates that the acetal molecule breaks up into three molecules.

The third experiment at the lowest temperature was so slow that complicating reactions resulted, and the logarithmic graph showed a sharp break when half of the material had decomposed.

Methylal decomposed in the gas phase at 410° in a quartz vessel, doubling its pressure in about 50 minutes and then changing slowly without reaching equilibrium even after seven hours. An approximate constant of 0.03 was calculated from the slope of the logarithmic graph for the first half.

Isobutyl Chlorocarbonate

Isobutyl chlorocarbonate was found to decompose in a unimolecular manner at a low temperature. The material was obtained from the Eastman Kodak Co. The final pressure is more than twice the initial pressure and decomposition into three molecules is indicated. Although the $\log(P_f - P_i)$ graphs are quite straight, the reaction appears to be complicated. The data are summarized in Table V.

TABLE V

Decomposition of Isobutyl Chlorocarbonate

	Temp.	P_i	P_f	$t_{1/2}$	$t_{3/4}$	k
1	267°	150 mm	504 mm	160 min	380 min	0.0043 min^{-1}
2	302	500	1107	16	35	0.043

Conclusions

Many organic compounds decompose in the gas phase at easily measurable rates in the temperature range $300\text{--}400^\circ\text{C}$. Some of these are reactions of the first order.

In some cases studied here there is good agreement with the first-order equation, as indicated by the straightness of the line produced when $\log(P_f - P_i)$ is plotted against temperature. The line is often straight even up to 90 per cent completion. It must be emphasized, however, that agreement with the first-order equation does not necessarily permit the calculation of correct unimolecular constants. Reverse reactions and other complicating reactions sometimes act in such a way as to make the resultant of all the reactions appear to be first-order.

It will be noted that among related compounds the complex molecules decompose more rapidly than the simple ones—i.e. they reach a given specific reaction rate (k) at lower temperatures. For example the decomposition rate for propyl bromide at 360° is about the same as that for ethyl bromide at 390° . Ethyl iodide also decomposes at 360° with approximately the same rate as ethyl bromide at 390° . Acetal decomposes at 360° with about the same rate as methylal at 410° . Tertiary butyl chloride and isobutyl chlorocarbonate, with more complicated molecules, have comparable reaction rates at 315° and 300° .

In some cases the specific decomposition rate (k) was found to decrease

with pressure but the present data do not permit any theoretical interpretation of this fact. A considerable part of the decrease is due to the fact that two or more reactions are proceeding simultaneously.

Impurities often have a marked specific effect on the decomposition rate.

Caution must be used in the theoretical interpretation of reaction rates even if a smooth first-order equation is indicated.

The author wishes to express his indebtedness to Professor Farrington Daniels; and to the E. I. du Pont de Nemours Co. for a fellowship during a part of this work.

Summary

1. The rate of decomposition in the gas phase of thirteen organic compounds has been measured in the range 300-400°.
2. The decompositions were followed by measuring the pressure increases in all-glass and all-quartz vessels totally immersed in a thermostat.
3. The decomposition of ethyl bromide is an excellent unimolecular reaction.
4. Gaseous n-propyl bromide, iso-propyl bromide, ethyl iodide, acetal, and isobutyl chlorocarbonate appear to follow the first-order equation in their decomposition. Some of these decompositions are undoubtedly unimolecular.
5. The decomposition of gaseous ethylene chloride, ethylene bromide, isopropyl chloride, tert-butyl chloride, ethylene chlorohydrin, and methylal are roughly first-order reactions but they are complicated.
6. The decomposition of gaseous chloroform is seriously complicated.
7. Precautions necessary in the interpretation of data of this type are emphasized.

Madison, Wis.

THE DEPOSITION OF COPPER IN THE PRESENCE OF GUM ARABIC¹

ROBERT TAFT AND OREN R. BINGHAM

In a previous paper² from this laboratory, an extensive study was made of the deposition of copper in the presence of gelatin. It was shown in this paper that the mass of the cathode deposit increased as the gelatin content of the plating bath became greater; that definite changes occurred in the form of the deposit as the gelatin content increased; and lastly, that gelatin produced a considerable increase in the cathode polarization as the current density was increased.

The experimental results obtained were interpreted to mean that gelatin is adsorbed upon the surfaces of the copper crystals as they are deposited, thus affecting the form of the deposit. Gelatin was chosen for the purposes of the original study, as it was a typical addition agent,³ the primary purpose of the investigation being to secure evidence for a satisfactory theory of addition agent action.

It is the purpose of this paper to present additional evidence for the theory of addition agent action proposed in our first paper; the evidence being secured by a study of the deposition of copper in the presence of gum arabic.

Our reason for choosing gum arabic was as follows: It has been suggested that an addition agent in order to be effective must itself be charged and migrate toward the cathode.⁴ If addition agent action is a question of adsorption only, its effectiveness might be more or less independent of its charge. With this in mind, we sought a material which could be used as an addition agent but which was known to migrate toward the anode. A study of the physico-chemical properties, including the electrical conductance, of gum arabic⁵ had been made in this laboratory. The results of this study had convinced us that gum arabic was an organic electrolyte and should properly be considered as a mixture of two salts, calcium arabate and magnesium arabate.⁶ If this be true, the large and complex anion, (i.e. the arabate), would upon electrolysis, migrate toward the anode. As it could scarcely be expected that

¹ Presented at the New Orleans Meeting of the American Chemical Society, March 30, 1932.

² Taft and Messmore: *J. Phys. Chem.*, **35**, 3585 (1931).

³ For a definition of addition agent consult Blum and Hogaboom: "Principles of Electroplating and Electroforming," 2nd ed., 102, (1930).

⁴ Frolich: *Trans. Am. Electrochem. Soc.*, **46**, 67 (1924).

⁵ Taft and Malm: *J. Phys. Chem.*, **35**, 874 (1931).

⁶ In addition to this evidence, Thomas and Murray: *J. Phys. Chem.*, **32**, 677 (1928), have shown that gum arabic, freed from metals by electrodialysis, is an acid which is not amphoteric.

a negative ion would be adsorbed by the negatively charged cathode,¹ any adsorption of gum arabic upon copper, if shown, would presumably be that of the undissociated gum arabic.

For this reason, as well as the added reason that no systematic studies of gum arabic as an addition agent for copper plating baths were available in the literature, we decided to carry out an investigation somewhat similar in scope to the study reported for gelatin and copper deposition, replacing the gelatin with gum arabic.

The gum arabic used was purified according to the method described by Taft and Malm.² The material used had a moisture content of 10.5% as determined by drying to constant weight at 100°C. Its ash content was 3.1% on a moisture-free basis. The remaining materials, copper sulfate and sulfuric acid, were the c.p. grade of a well-known manufacturer.

The experimental procedure was, in the main, similar to that used by Taft and Messmore.³ A number of electrolytic cells were connected in series with suitable coulometers, a variable resistance, and a source of direct current. The electrolytic cells consisted of 150 cc. pyrex beakers (containing 100 cc. of electrolyte); a platinum cathode and a copper anode, which had previously been given a heavy plate of copper electrolytically, were used to conduct the current to and from each cell.⁴ The electrodes in all cells were cut to the same size and were approximately 2.5 cms. on an edge. Electrolysis in the test cells was carried out at constant temperature, the constancy of temperature being secured by placing the cells in a constant temperature bath whose temperature fluctuations were less than 0.1°C. The coulometer used as reference was a copper coulometer employing as electrolyte, copper sulfate, alcohol, and sulfuric acid in the proportions recommended by Oettel.⁵ The coulometers, in duplicate or triplicate, were always run in an ice bath, it having been found⁶ that the mass of copper deposited from such a bath gave results more consistent with the standard silver coulometer.

In most of our solutions, pH measurements were made. As has been previously pointed out (Taft and Messmore) these serve chiefly to indicate

¹ In this connection, however, one should recall that the increased stability of negatively charged colloidal particles, which results in certain cases when electrolytes are added, is explained by the assumption that the negatively charged particle is increasing its negative potential. This increase in potential, it is assumed, results from the adsorption of negative ions by the negatively charged body. (cf. Bancroft: "Applied Colloid Chemistry," 2nd ed., 294 (1926).) If this assumption is correct, by analogy, it would be possible for a negatively charged surface to adsorb the negative gum arabic particles. Evidently in this case it would be the relative "negativeness" which would determine whether adsorption occurred or not.

² Loc cit.

³ Loc. cit.

⁴ The electrodes in each cell were equally spaced at approximately 3 1/2 cms. apart. A clearance of 2 cms. was left between the bottom of each electrode and the bottom of the beaker to allow complete settling of the anode mud.

⁵ Chem. Ztg., 17, 543 (1893). Matthews and Wark, (J. Phys. Chem., 35, 2345 (1931)) have called attention to the doubtful value of alcohol in the copper coulometer bath. Extensive investigation of the effect of alcohol in such baths, now under way in this laboratory, confirms the work of Matthews and Wark. We have continued to use alcohol, however, as our early trials were made before this information was available.

⁶ Taft and Messmore: unpublished data.

an additional characteristic of these baths, and in addition are of some value in interpreting our results, particularly with respect to the formation of copper oxides. The pH values were determined at 26°C by the use of the quinhydrone and saturated calomel electrodes, employing the equation:

$$\text{pH} = \frac{0.7177 - 0.00074 \times t - 0.2458 - E_c}{0.0001983 T}$$

where E_c was the observed potential of the cell, quinhydrone electrode—solution—calomel electrode, t , the temperature of determination on the Centigrade Scale, and T , the absolute temperature.

Data was obtained upon the mass, form and copper content of cathode deposits over a range of concentrations and temperatures. Analysis for copper of the cathode deposits was made according to the procedure described by Taft and Messmore.

After some preliminary trials, in which the mass of the cathode deposit was found to vary in an apparently erratic fashion with gum content, a series of cells was used at the same gum content, but of varying copper sulfate concentration, the remaining conditions being constant, i.e. 30°C and at a current density of 2 amperes per square decimeter.¹ The results of this run are given in Table I.

TABLE I

Mass of Cathode Deposits in Presence of Gum Arabic, Gum Content
0.25 gm/100 cc. solution

Concentration of copper sulfate	0.25 M		0.50 M			
	1	2	1	2		
Mass of Deposit, grams	0.5197	0.5200	0.5206	0.5205		
Excess Weight, grams	0.0117	0.0120	0.0126	0.0125		
Concentration of copper sulfate	0.625 M		0.75 M		0.875 M	
	1	2	1	2	1	2
Mass of Deposit, grams	0.5170	0.5178	0.5143	0.5140	0.5115	0.5122
Excess Weight, grams	0.0090	0.0098	0.0063	0.0060	0.0035	0.0042
Concentration of copper sulfate	1.0 M		1.25 M			
	1	2	1	2		
Mass of Deposit, grams	0.5090	0.5093	0.5088	0.5087		
Excess Weight, grams	0.0010	0.0013	0.0008	0.0007		
Coulometer						
	1		2			
Mass of Deposit	0.5078		0.5083			

¹ All current densities stated in this paper are calculated on the basis of one side of the cathode alone. Actually copper is deposited upon both sides, although not as extensively on the rear side as on the front. The current densities actually employed were, therefore, between 2/3 and 1/2 the values given.

The excess weights tabulated above were obtained by subtracting the average mass of the two coulometer deposits from the mass of the cathode deposit. This excess, as will be shown, is due to the inclusion of oxides of copper and of gum arabic or its hydrolysis products. The above results showed that the maximum mass effect was obtained in the cells having a copper sulfate concentration of 0.5 molar. As the effect was small at best, most of our subsequent studies were carried out at this concentration of copper sulfate.

In order to show that the gum arabic does affect the mass of the deposit, however, it was necessary to show the effects of varying the copper sulfate concentration upon the mass of the cathode deposit in the absence of gum arabic. With this object in view, the above run was duplicated with the exception of the addition of gum arabic. The results obtained for this run are shown in Table II.

TABLE II¹

Mass of Cathode Deposits in Absence of Gum Arabic

Concentration of copper sulfate	0.25 M		0.50 M			
	1	2	1	2		
Mass of Deposit, grams	0.5203	0.5206	0.5205	0.5217		
Excess weight, grams	0.0028	0.0031	0.0030	0.0042		
Concentration of copper sulfate	0.625 M		0.75 M			
	1	2	1	2		
Mass of Deposit, grams	0.5213	0.5214	0.5214	0.5214		
Excess weight, grams	0.0038	0.0039	0.0039	0.0039		
Concentration of copper sulfate	0.875 M		1.0 M		1.25 M	
	1	2	1	2	1	2
Mass of Deposit, grams	0.5208	0.5203	0.5216	0.5213	0.5194	0.5204
Excess weight, grams	0.0033	0.0028	0.0041	0.0038	0.0019	0.0029
	Coulometer					
	1		2			
Mass of Deposit	0.5176		0.5174			

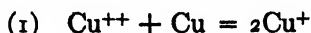
The average excess weights are in all solutions, save the most concentrated, between three and four milligrams. Variations are undoubtedly due to two factors:

(1) The variation of hydrolysis with concentration, which, in the more dilute solutions, would produce relatively more copper oxide. Upon formation and adsorption such oxide (or hydroxide) would tend to increase the mass of the cathode deposit as already shown by Richards, Collins and Heimrod.² It should be noted, however, that while the percentage hydrolysis increases with dilution, the concentration of cupric oxide would be the product of the fractional hydrolysis by the concentration of the salt. Without doubt this product reaches a maximum, not in the most dilute solution, but in some concentration of salt intermediate between the values employed, i.e. between 0.25 M and 1.25 M.

¹ Temp. 30°C; current density, 2 amperes per square decimeter.

² Proc. Am. Acad. Arts Sci., 35, 123 (1899).

(2) To the increased solvent action of the copper sulfate solution, as its concentration increased, upon metallic copper. Such solution takes place presumably (cf. Richards, Collins and Heimrod) according to the equation:¹



The point of immediate concern, however, is the effect of gum arabic upon this excess weight. Comparison of the deposits at a copper sulfate concentration of 0.5 M from Tables I and II, shows that the excess weight is some three to four times as great in the presence of gum arabic as it is in its absence.²

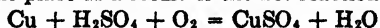
The difference between the excess weights in the two sets of experiments (at 0.5 M) cannot immediately be said to be due to inclusion of gum arabic alone. It might be reasoned, and with some justification, that the gum arabic disturbs the ratio $\text{Cu}^{+++}/\text{Cu}$ in favor of cuprous ion, thus producing more cuprous oxide which presumably could increase the mass of the deposit, as suggested above. Or possibly, the increased cuprous ion concentration would favor the discharge of the cuprous ion, thus producing a greater mass of copper than in the coulometer deposit. We have endeavored to determine in two ways if these factors are the prevailing ones:

(a) To determine the reducing action of the gum arabic used upon copper sulfate;

(b) To analyze the cathode deposits for copper, the results of which are discussed later in this paper.

To determine the visible extent of the reducing properties of gum arabic, 0.5 gm. were treated with Fehling's solution, according to the directions of Quisumbing and Thomas.³ With our purified material no cuprous oxide was visible upon several trials after long standing, indicating complete absence of reducing action.

¹ Solution may also take place as a result of the net reaction:



(Cf. Mellor: "Treatise on Inorg. Chem.," 3, 87). We have found, as a result of a large number of trials, that deposits from "neutral" (see Table VII) copper sulfate, or from solutions deliberately acidified with sulfuric acid, are always heavier when deposited from an electrolyte which has been deoxygenated by bubbling an inert gas through the solution before electrolysis and protecting such cells from atmospheric oxygen during electrolysis. Comparison with similar cells, run under otherwise similar conditions but not so treated, shows that the differences are small, and further depend, as is to be expected, upon the concentration of sulfuric acid and copper sulfate. The differences between such deposits are rarely greater than two or three tenths of a milligram in a deposit of 0.5 gram, obtained as a result of approximately a four hour run. The increased weight (in the absence of oxygen) may also be due, in part, to the absence of oxidation of cuprous ion. In the presence of oxygen such oxidation would cause increased solution as indicated by equation (1). In any case the effect of oxygen (both in cells containing gum arabic and in those free from this substance) is small compared to the effect noted above, so that we have made all electrolyses reported in this paper in air.

² Strictly speaking, the two runs are not directly comparable, as the quantities of electricity passed through the two sets of solutions are not the same. Multiplying the excess weights by the ratio of the coulometer deposits reduces them to a more nearly comparable basis. From the standpoint of the above argument the deposits are comparable as the differences of the coulometer deposits in the two trials are slight.

³ J. Am. Chem. Soc., 43, 1503 (1921).

We next determined the effect of varying the gum arabic content upon the mass of the cathode deposit, keeping the copper sulfate content of the solutions constant at 0.5 M for the reason stated previously. The results of this run are given in Table III.

TABLE III

Mass of Cathode Deposit as a Function of Gum Arabic Content, grams.
Temp. 30°C—Current Density 2 amps./dm²

Gum arabic/100 cc. solution	0.		0.010			
	1	2	1	2		
Cathode Deposit	0.5004	0.4998	0.5059	0.5053		
Excess Weight	0.0035	0.0029	0.0090	0.0084		
Copper, upon analysis	0.4985	0.4986	0.5027	0.5023		
Excess copper	0.0018	0.0019	0.0060	0.0056		
Gum arabic/100 cc. solution	0.025		0.050			
	1	2	1	2		
Cathode Deposit	0.5075	0.5075	0.5091	0.5091		
Excess Weight	0.0106	0.0106	0.0122	0.0122		
Copper, upon analysis	0.5032	0.5030	0.5021	0.5024		
Excess copper	0.0065	0.0063	0.0054	0.0057		
Gum arabic/100 cc. solution	0.100		0.150		0.200	
	1	2	1	2	1	2
Cathode Deposit	0.5128	0.5121	0.5126	0.5137	0.5126	0.5126
Excess Weight	0.0159	0.0152	0.0157	0.0168	0.0157	0.0157
Copper, upon analysis	0.5042	0.5039	0.5036	0.5044	0.5031	0.5035
Excess copper	0.0075	0.0072	0.0069	0.0077	0.0064	0.0068
	Coulometers					
	1			2		
Cathode Deposit	0.4969			0.4969		
Copper, upon analysis	0.4966			0.4968		

The excess copper, tabulated above, is the difference between the copper found upon analysis of the cathode deposit in each test cell and the average of the two analyses for copper in the coulometer deposits, i.e. 0.4967 gm. As will be seen, the excess copper is sensibly constant around 6 mgm. for all cells containing gum arabic, with a slight tendency to increase in the cells containing the largest quantities of gum arabic.

In this connection, it might be mentioned that increasing the gum content greatly beyond a concentration of 0.25 grams per 100 cc. of solution led to erratic results, as will be seen by an examination of Table IV.

TABLE IV

Mass of Cathode Deposit as a Function of Gum Arabic Content, grams.
Temp. 30°C; Current Density 2 amps./dm²

Gum Arabic/100 cc. solution	0.25		1.5	
	1	2	1	2
Mass Deposit	0.5502	0.5496	0.5480	0.5703
Excess Weight	0.0171	0.0165	0.0149	0.0372
Coulometers				
	1	2		
Cathode Deposits	0.5329	0.5333		

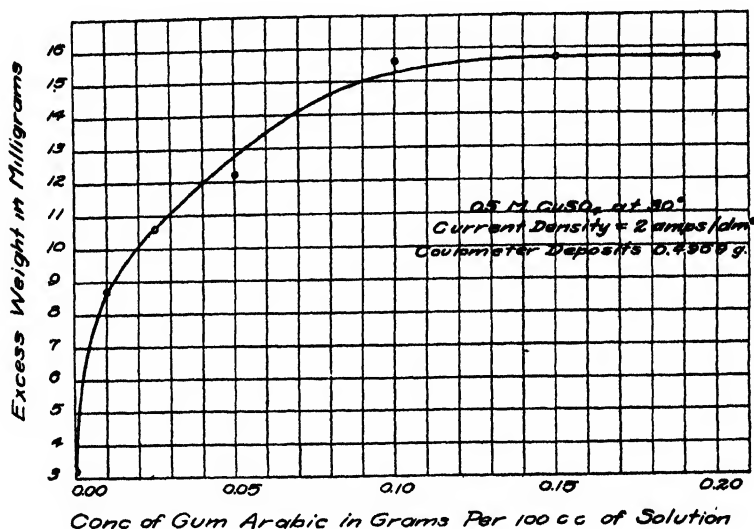


FIG. 1

The average of the two values obtained at 0.25 gm. agrees with the limiting value obtained in the data of Table III when multiplied by the ratio of the coulometer deposits. The two values obtained at 1.5 gm. (of gum arabic) show a very marked discrepancy. We finally traced this result to the fact that solutions containing 0.5 molar copper sulfate become saturated with calcium sulfate¹ when the concentration greatly exceeds 0.25 grams per 100 cc. of solution. The discrepancies are due then to the irregular mechanical inclusion or adsorption of the particles of calcium sulfate and its lack of adherence during the drying and weighing process.

To return to the data of Table III, however, it is apparent from considering the increase in excess weight that a limiting value is reached. This is seen more clearly in Fig. 1, where the excess weight is plotted as a function of gum concentration. The form of this curve resembles an adsorption curve

¹ Calcium sulfate is formed as the result of reaction between the ionizable calcium of the gum arabic (Cf. Taft and Malm, loc. cit.) and the high concentration of sulfate ion from copper sulfate.

and we are, therefore, assuming that this excess weight has been adsorbed upon the surface of the depositing copper crystals. As has been pointed out by Taft and Messmore, the justification for such an assumption is this: the masses of copper in this series of trials are sensibly the same. Ordinates would, therefore, represent amount adsorbed per unit mass, the unit mass being taken as the mass of the coulometer deposit. The difference to be noted, as suggested by Taft and Messmore, between this series of trials and ordinary adsorption

experiments lies in the fact that the specific surface becomes greater, the greater the concentration of addition agent is. It should be stated that the differences in form here are considerably less than those which occur when copper is deposited in the presence of gelatin, i.e. the copper deposits do not reduce their crystal size as rapidly as with increased concentration of gelatin. The situation is further complicated by the fact that the nature of the surface also changes, as an examination of Fig. 2 will show.

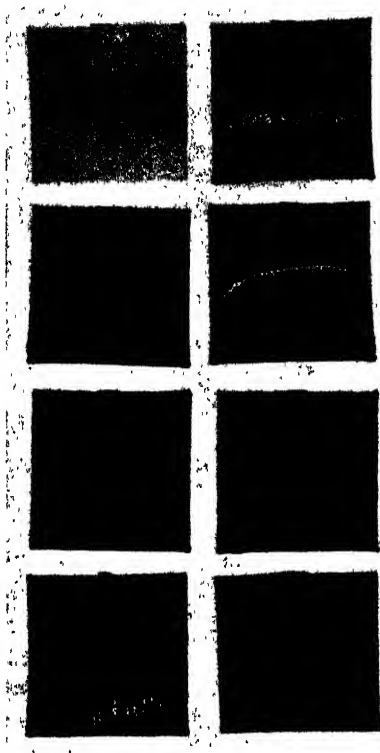


FIG. 2

Cathode deposits obtained from neutral copper sulfate in the presence of gum arabic. Concentrations of copper sulfate, left column, top to bottom, coulometer deposit, 0.25 M, 0.50 M, 0.625 M; right column, top to bottom, 0.75 M, 0.875 M, 1.00 M, 1.25 M. $\times 3/4$.

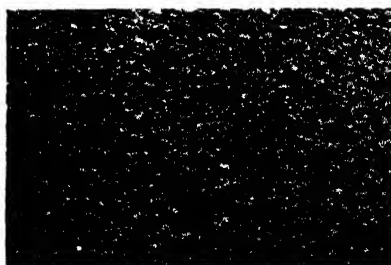


FIG. 2A

Photo-micrograph of dark area from electrode similar to those shown in Fig. 2. $\times 90$. Notice that the deposit, which is chiefly copper, shows no crystalline structure at this magnification.

While we are thus assuming that the total excess weight arises as a result of adsorption upon the crystals of depositing copper, it will become evident, we hope, that the gum arabic is adsorbed in two ways.¹ In order to show this

¹ That organic matter is actually present in such deposits we have shown qualitatively by heating such deposits in a stream of dry oxygen and collecting the issuing gas in a solution of barium hydroxide. The production of barium carbonate is evidence that organic matter is present. Controls give no appreciable deposit of the carbonate.

it will be necessary to examine our analytical data. Consider, for example, the data of the first four cells (Table III), i.e. those containing no gum and those containing 0.010 gm. per 100 cc. It will be noted that the addition of the gum produces approximately a threefold increase in the excess copper. This increased mass of copper in such deposits might arise from one or more of the following effects produced by the gum arabic:

- (1) Increase in the concentration of Cu^+ and its subsequent discharge.
- (2) Increasing adsorption of cupric oxide which may be formed as a result of hydrolysis of copper sulfate. This increased adsorption of cupric oxide might be due to an increase in the concentration of this oxide, or to an increase in the effectiveness of the adsorbent.

- (3) Increase in the adsorption of cuprous oxide for reasons similar to those suggested under cupric oxide.

- (4) Adsorption of copper arabate, which is undoubtedly present, as a result of the formation of calcium sulfate described previously.

- (5) Inclusion of copper from the anode "mud". This "mud" always contains free copper in considerable proportion which is formed by mechanical disintegration of the anode. It is present in somewhat greater amounts in baths containing gum arabic than in those which do not. We do not believe that this source of copper is to be seriously considered as affecting the mass of copper in the cathode deposit. The "mud" falls very directly to the bottom of the cell beneath the anode and forms a deposit with fairly sharp edges, which indicates that the particles in the mud are nearly uniform in size; since the nearest edge of this deposit is some 4 cm. from the cathode, it is not likely that any appreciable amount of copper is taken up by the cathode from this source. Furthermore, this copper has little tendency to adhere to the cathode, i.e. if the cathode deposit be stirred in the anode mud and then washed, there is no appreciable gain in weight. Of course, the correct experimental procedure would be to enclose the anode in a porous membrane, which would retain any mud formed. We have not done this for two reasons: (a) enclosing the anode in parchment paper or filter paper would likely introduce deleterious material from the paper. At least it has been found to do so in the silver coulometer. (Rosa and Vinal);¹ (b) the use of a porous cup around the anode, we felt, was precluded because of the considerable difference in concentration of copper sulfate produced in the anolyte. As we were using solutions only 0.5 M originally, the concentration effect might be of greater magnitude than the effect of the gum arabic. It may be recalled, too, that the silver coulometer employing a glass dish beneath the anode to catch the "mud" gives the same results as the silver coulometer employing a porous cup. (Rosa and Vinal: loc. cit.). Evidently, in the case of silver, there are no finely divided particles of the anode mud which reach and adhere to the cathode. In the case of our cells, the anode mud settles very rapidly and leaves a deposit, as we have already pointed out, with *sharp* edges immediately below the anode.

¹ Bureau Standards Bull., 13, 479 (1917).

Of the possibilities listed above to account for the increased copper, we are inclined to regard the second and third points as the probable ones, although the first and fourth may be concerned to a slight extent. Our reasons for discarding the first of the possibilities listed above are that the gum arabic used, as has been pointed out, has no visible reducing properties upon cupric ion in alkaline solution and would likely have a smaller reducing ability (if it possesses any at all) in the slightly acid solutions with which we worked. (See Table VII). More important than this, however, is the appearance of our deposits. An inspection of Figs. 2, 4 and 6 shows that the deposits are quite dissimilar. If the excess weight were copper from cuprous ion, it should still have the appearance of copper, which it does not. This variation of form we have considered in greater detail below.

On the other hand, deposits of copper obtained in the presence of considerable sulfuric acid and gum arabic have excess weights as is shown by the data of Table V.

TABLE V

Excess Weights in Presence of Sulfuric Acid (1N), grams
0.5 M CuSO_4 , 30°C and 2 amp./dm²

Gum Arabic per 100 cc. solution	Coulometer		0.		0.01	
	1	2	3	4	5	6
Mass of deposit	0.4702	0.4704	0.4693	0.4692	0.4695	0.4693
Excess Weight	—	—	—	—	0.0003	0.0001
Gum Arabic per 100 cc. solution	0.025		0.050		0.10	
	7	8	9	10	11	12
Mass of deposit	0.4695	0.4695	0.4694	0.4700	0.4699	0.4700
Excess Weight	0.0003	0.0003	0.0002	0.0007	0.0007	0.0008
Gum Arabic per 100 cc. solution	0.150					
	13	14				
Mass of Deposit	0.4699	0.4701				
Excess Weight	0.0007	0.0009				

In sulfuric acid of this concentration there is little or no possibility of oxide formation and we are, therefore, assuming that the excess weight is due to adsorption of gum arabic. It will be noted that the excess weights of Table V are very small. Due to the increased solvent action and the absence of any oxide in these acid solutions, the deposits of copper obtained in the absence of gum arabic are lighter than those obtained in the coulometers. For this reason the excess weights have been calculated by taking the difference between the mass of the deposits obtained in the presence of gum arabic and the control. That the effect of increasing the gum arabic content is to increase the amount of gum arabic adsorbed upon the copper is shown by plotting the data of Table V, which has been done in Fig. 3. The evidence here, we believe, is quite conclusive, as there seems to be no other way by which the gum arabic could be found in the deposit. We have demonstrated

the presence of organic matter in deposits obtained from these acid solutions of copper sulfate in the same way as described in Footnote 1, p. 2345, i.e. by passing oxygen over the heated deposit and collecting the gases in barium hydroxide solution. Controls give no appreciable deposit of barium carbonate, while those deposits formed as above described give a measurable quantity. The possibility of the formation of a complex cation of gum arabic and copper can be dismissed for two reasons: (a) complex cations are not formed, as a rule, from complex anions and simple cations; (b) when one recalls the carbo-

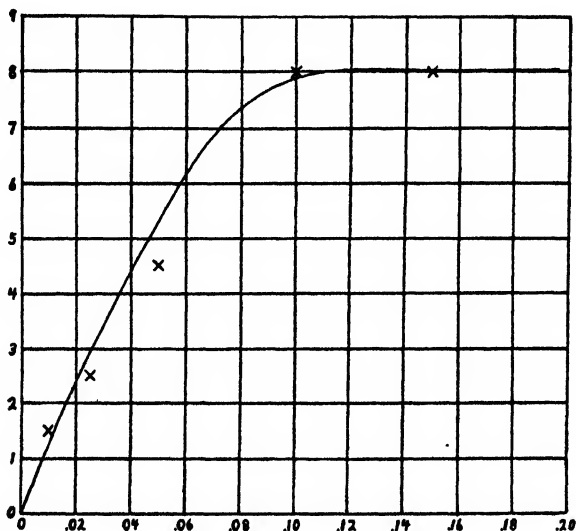


FIG. 3

Excess weights in presence of sulfuric acid and gum arabic. Ordinates, Excess Weight in Tenths of Milligrams; Abscissae, Grams of Gum Arabic per 100 cc. Solution.

hydrate-like character of gum arabic, any complex ion formation would undoubtedly produce a complex *anion* rather than a cation.

The form of the deposits obtained from an acid bath in the presence of gum arabic is shown in Fig. 4 (deposit from cell No. 13, Table V). The micro-structure of these deposits shows that the adsorption of gum arabic produces a considerable distortion of the copper crystals, as is shown in Fig. 5.

Considerable information as to the nature of the excess weight can be obtained by comparing Fig. 4, the deposit of copper obtained in the presence of gum arabic in an acid bath, with the form of the deposit obtained from "neutral" copper sulfate in the absence of gum arabic (Figs. 6 and 7). It will be noted that the deposits are not greatly different in form (Figs. 4 and 6). Both are apparently crystalline and are copper colored. Both, however, show excess weight; the deposit from the acid bath showing an excess weight as a result of adsorption of gum arabic; that from the neutral bath being heavier due to inclusion of copper oxides. When both gum arabic and copper oxides are present, there is a marked increase in the excess weight, as has been

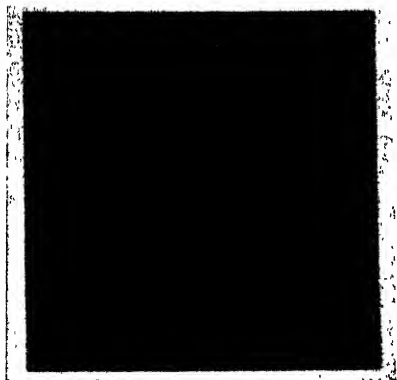


FIG. 4

Cathode deposit from solution containing 0.5 M CuSO_4 , 1 NH_2SO_4 , and 0.025 gm. of gum arabic per 100 cc. solution. Temperature 30°C ; current density, two amperes per square decimeter. $\times 1.7$.

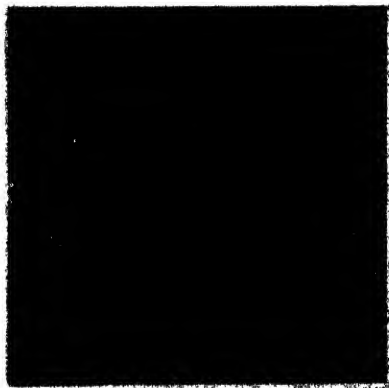


FIG. 6

Cathode deposit from neutral copper sulfate, absence of gum arabic. 0.5 M CuSO_4 ; 30°C ; 2 amperes per square decimeter.



FIG. 5

Photo-micrograph of an area from electrode shown in Fig. 4. $\times 28$. The "wrinkled" appearance of the copper crystals is due apparently to their displacement as they are deposited, i.e. the "wrinkles" in cross section appear as a series of steps.



FIG. 7

Photo-micrograph of an area from electrode shown in Fig. 6. $\times 30$.

pointed out, and further, a marked difference occurs in the form of the deposit, as can be seen by inspection of Fig. 2. Before we "explain" the form of these deposits (in Fig. 2), we must consider the evidence for the presence of the copper oxides. That such substances are present in small quantities is not open to question. Richards, Collins and Heimrod have established the evidence for the presence of cuprous oxide. This comes as a result of the reaction already formulated in equation (1) and the subsequent hydrolysis of cuprous sulfate.

These investigators apparently overlooked the possibility of the presence of cupric hydroxide (or oxide) in neutral copper sulfate solutions. As a re-

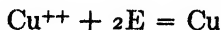
sult of our pH measurements, there can be little doubt that some cupric hydroxide is present. The data for the pH measurements is given in Table VI.¹ As can be seen, the gum arabic is with little effect upon the pH of the solution. If it be assumed that the sulfuric acid is completely dissociated, it is possible to calculate the approximate percentage hydrolysis of these solutions from the relation $\text{pH} = \log 10^\circ/xC$, where x is the percentage hydrolysis and C the concentration of copper sulfate in gram-equivalents per liter. Such a calculation gives 0.03% hydrolysis for the first two solutions listed in Table VI and only slightly less for the remaining ones. This would represent about 1.5

TABLE VI
pH Measurements of 0.5 M CuSO_4 at 26°

Grams of Gum 100 cc. solution	pH	Grams of Gum 100 cc. solution	pH
0.0	3.52	0.10	3.53
0.01	3.52	0.15	3.53
0.025	3.53	0.20	3.53
0.05	3.53	0.25	3.53

milligrams of cupric hydroxide per 100 cc. of solution. This value seems reasonable, in spite of the likely error introduced by the high concentration of salt as mentioned above, as O'Sullivan² obtained a value of 0.07% for the hydrolysis of $N/10 \text{ CuSO}_4$ at 18°.

Bearing more directly upon the inclusion of cupric oxide is the fact that the ratio excess copper/excess weight of the deposits obtained from "neutral" copper sulfate averages around 0.65. Thus, if these ratios are taken from the data of Tables III and VII, they are found to be 0.56, 0.66, 0.67, 0.62, 0.71 and 0.67. The only one left out of consideration is the data of the cell electrolyzed at 0° which obviously is in error. When the errors involved in determining a small quantity by the difference of two relatively large ones are considered, the agreement is surprising. The average of the above values is 0.65 which is that of the ratio $\text{Cu}/\text{Cu}(\text{OH})_2$. Some caution should be observed in drawing the conclusion that the only compound included in such deposits is $\text{Cu}(\text{OH})_2$, however, as we are not certain how much of the copper results from electrolysis; that is, how much is produced as a result of the reaction:



The uncertainty is produced, as has already been pointed out, as a result of a re-solution of part of the copper and of the possible discharge of cuprous ion.

¹ These pH values are likely in error due to the salt effect for which no correction has been made. It is quite probable that the activity coefficients of quinone and hydroquinone will be appreciably different in our relatively concentrated solutions than in pure water. (Clark: "Det. of Hydrogen Ions," 3rd ed., 408.) However, we are more concerned with the relative effect in the copper sulfate solutions without and with the presence of gum arabic.

² Trans. Faraday Soc., 21, 319 (1025).

Likely then, both oxides of copper are present, the relative proportion of which will be determined by the concentration of the copper sulfate; the amount of cupric hydroxide increasing with dilution; the amount of cuprous oxide increasing with increasing concentration of copper ion, as inspection of the equilibrium equation for solution of metallic copper shows. Since both hydrolysis and rate of solution increase with rising temperature, the amounts of these oxides will increase at higher temperatures.¹

We believe that the presence of these oxides accounts for the form of the deposits as illustrated in Fig. 2. In the more dilute solutions (0.25 and 0.50 M) hydrolysis is relatively extensive and there is thus considerable cupric oxide present. This, we are assuming, is present in sufficient proportion at these dilutions to allow its simultaneous adsorption with the gum arabic, giving rise to the dark colored deposits. In the more concentrated solutions (0.625 M and greater) the catholyte requires dilution (which results from the deposition of copper upon the face of the cathode) before sufficient oxide is formed. As the rising catholyte is depleted of its copper, a concentration is eventually reached at which the amount of cupric oxide formed is sufficient to be visibly adsorbed. As the concentration of copper sulfate is increased, the level at which hydrolysis will furnish sufficient oxide to give the dark colored deposit becomes higher and higher, as our photographs show.² It is not solely a question of hydrolysis, however. For, if such were the case, there would be a *gradual* darkening of the color of the deposit as it rises higher and higher on the cathode. An inspection of the deposits shows that the dividing line between the dark colored material and the lighter colored copper is quite sharp. Further, it has been found that for the same concentration of copper sulfate, an increase in the gum arabic content produces the dark colored area at a lower level. It appears as if a factor related to a solubility product is involved, i.e. when $C_{\text{gum}} \times C_{\text{oxide}}$ (C 's representing concentrations) exceeds a certain value the dark colored material is produced. Possibly the colloidal cupric hydroxide reacts with gum arabic³ at the surface of the cupric hydroxide micellae, forming copper arabate. This material, it might be assumed, is more powerfully adsorbed than either cupric hydroxide or gum arabic singly. It must be admitted that the possibility of inclusion of the gum arabic—cupric hydroxide complex might take place as the result of a charged colloidal

¹ The remaining possibility of those listed on page 2346, i.e. that the excess weights in the presence of gum arabic in "neutral" solutions of copper sulfate may be due to adsorption of copper arabate *alone*, is eliminated for several reasons: The excess copper could not be accounted for on the basis of such a compound (and likely of any adsorption complex) as the copper content of such a compound is probably less than 3%. This figure is based on the approximate equivalent weight of gum arabic of 1200 and the monobasic character of the free acid, as established by Thomas and Murray (loc. cit.). The per cent of excess copper in the excess weights of such deposits is invariably many times higher than this. (Cf. Table III). Further, it is not constant at constant temperature and increases as the temperature rises. (Cf. Table VII).

² The dark-colored deposits grow from the bottom of the cathode up and not from the top down, as Fig. 2 might lead one to believe. We hope to publish shortly a study of the growth of such deposits.

³ That gum arabic is taken up at a solid interface is shown by the rather marked protective ability of gum arabic. Zsigmondy (Z. anal. Chem., 40, 697 (1901)) has shown, for example, that gum arabic has a relatively small gold number.

particle. Undoubtedly colloidal cupric hydroxide formed in a solution containing a high concentration of cupric ion will be positively charged. The fact that there is no diminution in total copper after the formation of the dark areas, taken together with the form of our excess weight curve, is the argument against this view. Our original intention of showing adsorption by a

TABLE VII

Mass of Cathode Deposit as a Function of Temperature, grams.

Current Density 2 amps./dm.²

Copper Sulfate, 0.5 M

Temp. °C	0°	0°	0°	0°	0°	0°
Grams of gum/100cc. sol.	0	0	0.01	0.01	0.15	0.15
Mass of Deposit	0.5180	0.5181	0.5197	0.5194	0.5314	0.5314
Excess Weight	0.0004	0.0003	0.00130	0.0010	0.0130	0.0130
Copper, upon analysis	0.5174	x	x	x	0.5209	0.5203
Excess copper	-0.0010	—	—	—	0.0025	0.0019
Temp. °C	40°		40°		40°	
Grams of gum/100cc. sol.	0		0		0.15	
Mass of Deposit	0.5293		0.5291		0.5464	
Excess Weight	0.0109		0.0107		0.0280	
Copper, upon analysis	0.5258		0.5250		0.5348	
Excess Copper	0.0074		0.0066		0.0164	
Temp. °C	60°		60°		60°	
Grams of gum/100cc. sol.	0		0		0.15	
Mass of Deposit	0.5482		0.5442		0.5578	
Excess Weight	0.0298		0.0258		0.0394	
Copper, upon analysis	0.5396		0.5358		0.5419	
Excess Copper	0.0212		0.0174		0.0235	

Coulometers

	1	2
Mass of Deposit	0.5182	0.5185
Copper, upon analysis	x	0.5184

x Analyses not made or lost.

neutral particle, however, is shown in the deposition of copper in the presence of gum arabic in *acid* solutions of copper sulfate. Here, we believe, there can be little question that the limiting value of excess weight is due to the adsorption of gum arabic.

That the composition of the adsorbed material varies with the temperature will be seen from the data of Table VII, which compares a series of cells, run under otherwise similar conditions at 0°, 40°, and 60°. As will be seen by a consideration of this data, the excess weight increases with rising temperature, but the excess copper increases more rapidly than the excess weight.

The inference to be drawn from this set of data is that the proportion of organic matter in the deposit increases as the temperature is lowered. That is,

if one takes the difference between excess weights in baths containing gum arabic and those which do not (at the same temperature) these differences increase as the temperature is lowered. We feel, therefore, that our position with respect to the *adsorption* of both substances, i.e. copper oxides and gum arabic, is very securely fixed by this additional data.

The effect of temperature on the form of these deposits at various temperatures is worthy of note. These are illustrated in Fig. 8. The deposit obtained at 0° in the presence of gum arabic was one of the most striking of any of the hundreds of copper deposits made in this laboratory. In appearance it resembled a very highly polished bronze surface, but unfortunately, as far as

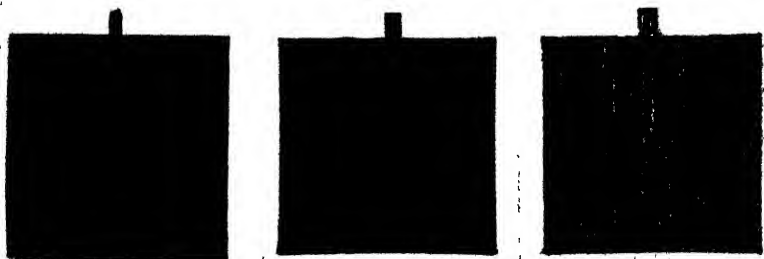


FIG. 8

Effect of temperature upon the form of the cathode deposit. Left to right, deposits obtained at 0°C , 40°C and 60°C . 0.5 M CuSO_4 , 15 grams of gum arabic per 100 cc. solution, 2 amperes per square decimeter. The deposit at 0° has the appearance of highly burnished bronze. $\times 1.1$.

any practical purpose goes, it was quite brittle. This deposit, it will be noted, was obtained when the proportion of organic substance in the deposit was the greatest. The deposit obtained at 40° (in the presence of gum arabic) was still smooth, but rather grainy. The deposit obtained at 60° (in the presence of gum arabic) was highly striated, the striae standing out as deep ridges, the area between the ridges being barely covered by a deposit of lighter colored "copper." This deposit contained the greatest proportion of copper oxides, both of which are very much poorer conductors of electricity than is copper itself. We plan, in another paper to be published shortly, to discuss the growth of such striated deposits in somewhat greater detail.

Summary

1. The mass of cathode deposits in the presence of gum arabic, both in neutral and acid solutions of copper sulfate, increases with increasing concentration of gum arabic to a limiting value.
2. Cathode deposits in neutral copper sulfate solutions contain more copper than is obtained in a copper coulometer placed in series with such baths, the proportion of such "excess copper" increasing with rising temperature.
3. We interpret our results to indicate that copper oxides (both cuprous and cupric) and gum arabic are *adsorbed* simultaneously upon the surface of the newly deposited copper crystals obtained upon electrolysis of neutral copper sulfate solutions; from acid solutions gum arabic alone is adsorbed.

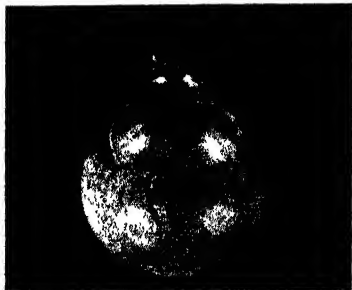
THE RHYTHMIC CRYSTALLISATION OF MELTS

Part. I. A Preliminary Investigation of the Factors influencing the Phenomenon

BY JOHN FREDERICK JAMES DIPPY

The phenomenon of rhythmic crystallisation of molten substances in thin films has been observed in the following instances: mannitol, and ammonium lithoxanthate;¹ ethyl tetracarbethoxylate, benzophenone and coumarin;² sulphur;³ p-ethoxybenzylideneaminophenylpropionic acid,⁴ salol, methyl salicylic acid, and p-toluenitrile;⁵ myristic, lauric, undecic and decic acids;⁶ antipyrine, sulphonal, malonamide, benzoin, benzonaphthol, santonin, m-diethylaminophenol, diamionaphthalene, asparagine salts, benzoic acid, salicylic acid and hippuric acid;⁷ benzil, menthol, acetanilide and m-dinitrobenzene.⁸

The author finds that the phenomenon is also exhibited by piperonal, terpin hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol and 3:5-dichloro-4-methyldiphenyl (the preparation of this compound will be described in a separate publication).



PHOTOGRAPH I

A preliminary investigation of the factors controlling the phenomenon has been made by the author. The most suitable substance for examination was found to be 3:5-dichloro-4-methyldiphenyl, since it crystallises rhythmically so readily and in such well defined fashion. This substance was noticed to exhibit the phenomenon, when in its preparation, a flask containing the molten

compound upon its walls was allowed to cool. After considerable supercooling rhythmic crystallisation occurred (see photograph 1).

Rhythmic Crystallisation upon Slides

The crystallisations of the melts were performed upon glass microscope slides which had been specially cleaned by immersion in nitric-chromic acid

¹ Brewster: Trans. Roy. Soc. Edinburgh, 20, 607 (1853).

² Alexéeff: J. Russ. Phys.-Chem. Soc., 38, 1120 (1906).

³ Fischer-Treuenfeld: Kolloid-Z., 16, 109; Köhler: 17, 10 (1915); Hughes: Nature, 123, 603 (1929).

⁴ Vorländer and Ernst: Z. physik. Chem., 93, 521 (1919).

⁵ Schubert: Kolloid-Z., 35, 219 (1924).

⁶ Garner and Randall: J. Chem. Soc., 125, 369 (1924).

⁷ Bernauer: Neues Jahrb. Mineral. Geol., 56, 342 (1927).

⁸ Hedges: Nature, 123, 837 (1929).

mixture for three months, then washed several times with distilled water and steamed. The slides were stored in a calcium-chloride desiccator until perfectly dry. A flat iron bar over a small Bunsen burner flame was used for heating the slides. In order to procure a melt of a substance upon a slide, the latter was quickly transferred to the bar, which recorded a temperature about 20°C above the melting point of the substance. A small quantity of the substance was then added to the slide and the melt so produced was spread in a thin film by use of a clean glass rod. The slide was then placed upon a sheet of asbestos in an empty desiccator and allowed to cool, the interference of impurities and dust particles being thus largely eliminated.



PHOTOGRAPH 2
(Actual size)



PHOTOGRAPH 3
(Actual size)

In this manner thirty different organic compounds were allowed to crystallise spontaneously from their melts. In the majority of cases crystallisation was continuous, but in the instances already cited the rhythmic phenomenon was manifested.

Rhythmic growth invariably begins with the appearance of one or more nuclei which gradually extend radially in all directions for some distance; then there follows an abrupt arrest in growth, after which crystallisation extends once more into the melt. This pulsation of crystallisation proceeds regularly until the melt is completely solidified. The result is a series of concentric bands of solid separated by what appear to be gaps (see photographs 1 to 5).

Phenanthrene and cinnamic acid yield minute bands of crystals best observed under a lens. Thymol crystallises in plates but gives evidence of definite pulsations of growth although not of the common banded form. Piperonal, terpin hydrate, vanillin, phenyl benzoate and 3:5-dichloro-4-methyldiphenyl all gave bands easily observed by the naked eye. The regular manner in which 3:5-dichloro-4-methyldiphenyl crystallises is depicted in photograph 2. The growth began from opposite corners; the junction of the two waves is well defined. Photograph 3 is a side view of the same slide, showing the bands approaching the centre from either side in "drift" formation. In all the following text the compound under investigation is 3:5-dichloro-4-methyldiphenyl, except where stated otherwise. The specimens used had been recrystallised two, three and four times from absolute alcohol, and stored for three months in a vacuum desiccator before being used. Identical results were achieved by employing any of the three specimens.

The Effect of Supercooling

It was noticed that where rhythmic crystallisation occurred, the film of melt had been allowed to crystallise spontaneously. Hence almost invariably the melt had supercooled considerably before crystallisation began. In order to discern if this were a factor contributing to the phenomenon, films which had spontaneously crystallised rhythmically were melted afresh and allowed to cool. At frequent intervals the melts were inoculated with some of the solid so as to prevent supercooling. In all cases continuous crystallisation resulted. Forty observations were made, yielding the same result.



PHOTOGRAPH 4
(1/2 actual size)

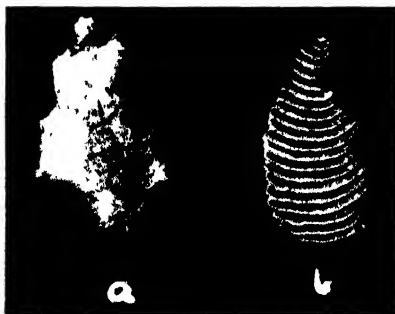
The different results obtained with and without supercooling are shown in photograph 4. Two films of melt were allowed to crystallise side by side on the same glass slip; film (a) was inoculated to prevent supercooling, and film (b) crystallised spontaneously. The experiment was repeated several times and the same result obtained.

When supercooling was small it was observed that the melts crystallised in a small number of unusually wide bands. Thus it would appear that the degree of supercooling is a factor essential to the production of rhythmic crystallisation in a molten substance. The relation between the degree of supercooling and the frequency of the crystal bands has not yet been ascertained. It is hoped later to study this further.

It was emphasised by Alexéeff¹ that supercooling is a factor upon which depends the rhythmic crystallisation of the substance he investigated.

The Effect of an Air Interface

The presence of an air interface is another factor controlling the appearance of rhythmic crystallisation. On a large slide two independent films of 3:5-dichloro-4-methyldiphenyl were, in the one case (6), left exposed to the air, and in the other case (a), covered by a clean glass cover-slip. Upon cooling, both films crystallised spontaneously, (a) did so in continuous fashion, and (b) in rhythms, (see photograph 5). This experiment was repeated a large number of times and always proved reproducible.



PHOTOGRAPH 5
(1/2 actual size)

Further evidence for the air interface factor is supplied by the following experiment. A film of the melt was partly covered with a glass slip and al-

¹ Alexéeff: loc. cit.

lowed to supercool. When the air exposed portion of the film crystallised first it did so rhythmically, but upon extending into the region contained between the two glass interfaces, the growth immediately became continuous.

The dependence of rhythmic crystallisation upon the presence of an air-interface was also noticed by Alexéeff.¹

The Effect of the Thickness of the Film

It was often found impossible to obtain a film of the melt of reasonably uniform thickness. This difficulty arose from the fact that upon cooling the slide, the surface tension of the melt increased and so caused the area occupied to diminish, but, on occasions, leaving behind an extremely thin film. Upon crystallising, these melts did so rhythmically in the portions of normal thickness, but the abnormally thin films crystallised continuously, even when inoculated by a growth of crystals from the rhythmic region.

It has also been observed that where rhythmic crystallisation occurs, the thinner the film the more rapid are the pulsations of crystal growth, that is, the narrower and more frequent are the bands; whilst on the same slide thicker portions of film crystallise with slower pulsations and consequent production of wider bands.

Repeated attempts were made at bringing about rhythmic crystallisation in melts contained in glass tubes of 5 mm. diameter (previously cleaned and dried in a manner similar to that employed for the slides) met with no success. In all cases crystallisation was continuous. Variations of degree and rate of supercooling appeared not to influence the mode of crystallisation. This result agrees with the behaviour of some unusually thick films of melt which crystallise spontaneously in continuous form.

It seems, therefore, that film thickness is a factor influencing rhythmic crystallisation. Measurements already made point to there being definite limits of thickness of film within which rhythmic crystallisation can occur. However, the author proposes to investigate this factor in more detail.

The Nature of Rhythmic Growth

The pulsations of crystal growth in melts of 3:5-dichloro-4-methyldiphenyl have been closely examined. As seen from photograph 3, each band increases in height in the direction of its growth. This maximum height of growth is followed by what appears to be a gap, then begins the growth of the subsequent band.

The so-called gap when examined under a hand lens or a microscope, appears to be constituted of a very thin layer of crystals. This is depicted in photomicrograph 1 (taken with transmitted light). The bands of crystals appear dark, since they are comparatively dense,



PHOTOMICROGRAPH 1
($\times 30$)

¹ Alexéeff: loc. cit.

whereas the interim space between the consecutive bands stands out bright and shows the needle-like crystals aligned in the direction of radial growth.

Photomicrographs 2 and 3 illustrate the abrupt manner in which the growth of the bands begins and ends. Moreover, the peculiar "fan-like" growth of the crystals (noted also in certain observations made with the epidiascope) is well shown here. This "fan-like" growth extends with widening front in the direction of crystallisation.

The actual growth of crystals in a melt was followed upon a lantern screen with the aid of an epidiascope. This apparatus was fitted with a horizontal stage upon which was placed a slide containing a melt of 3:5-dichloro-4-



PHOTOMICROGRAPH 2
($\times 25$)



PHOTOMICROGRAPH 3
($\times 25$)

methyldiphenyl. The image of the slide, obtained with reflected light, was focussed upon the screen; this afforded a magnified view of the entire field of the melt. It was observed that when, after supercooling, a crystal nucleus formed, and had extended some distance, the melt rapidly flowed away in a wave, there followed a very short arrest and then the wave returned towards the ridge of crystals.

The rapid crystallisation of 3:5-dichloro-4-methyldiphenyl made it somewhat difficult to follow the features of the growth. More satisfactory results were achieved with piperonal and salol. The slow rate of crystallisation of these substances made them eminently suitable for the epidiascope investigation. Using these substances, the details of the growth have been more closely observed. In the supercooled melt a nucleus first forms, this extends radially thrusting out "fan-like" growths of crystals into the melt. Some of the melt becomes entangled in this network of crystals. While this crystallisation proceeds, the surrounding liquid recedes in a wave and then returns to the crystals bordering the first band, thus crystal growth begins once more in a very thin layer gradually increasing in thickness until the second band is complete. In some cases this thrusting out of "fan-like" growths causes the front of the crystallising band to be most irregular, whereas on the other hand, particularly in thick films, the growth is remarkably even (c.f. photomicrographs 2 and 3).

Rhythmic Crystallisation upon Evaporation of a Solution

Rhythmic crystallisation of 3:5-dichloro-4-methyldiphenyl has been effected by allowing thin layers of an ethereal solution of the substance to evaporate from a glass slide at room temperature. The appearance of rhythmic crystallisation after evaporation of solutions of various organic compounds has been previously observed by Kāgi,¹ and by E. C. H. Davies and his co-workers.²

Discussion

A number of attempts have been made to explain the phenomenon of the rhythmic crystallisation of melts.³ The majority involve the operation of capillary forces. The view put forward by Alexéeff is that upon the formation of a crystal nucleus in a supercooled melt, the heat produced by the crystallisation is adsorbed by the melt in the immediate vicinity of the nucleus and hence the surface tension between the melt and the crystals diminishes. The liquid consequently moves from the solid until, after cooling, the surface tension has increased sufficiently to allow the liquid to become attached once more to the solid. This theory involves only the capillary force exerted between the melt and the crystals. The capillary force existing between the melt and the slide is also a factor to be considered. In virtue of this force, the melt should tend to spread itself out more upon increase of temperature, and so ensure better contact with the solid. This factor appears, therefore, to militate against the theory advanced by Alexéeff. The explanation of rhythmic crystallisation given by Hughes is essentially the same as that of Alexéeff.

Vorländer and Ernst put forward a theory in which the capillary forces between melt and slide, and melt and crystals, are both taken into account, although no mention is made of the variation of these forces with changes of temperature. These workers state that the nucleus exerts capillary attraction upon the surrounding melt whereupon the latter rises in the crystal network and subsequently solidifies. When the height of the ridge has become so great that the adhesion of the melt to the slide overcomes its attraction to the crystal network there follows an inductive period. This theory is in agreement with observations made in this paper, but does not provide a complete explanation. It is true that solidification of the melt proceeds until an optimum height is reached; this it does in "drift" formation. Moreover, minute observation of the edge of a "drift" reveals that it consists of a bristling mass of needles protruding into the air; this constitutes the end of the crystal network. Crystallisation observed on the screen by means of the epidiascope evidenced the intrusion of a network of crystals into the melt, and also the moving away of a wave of the latter from the solid, which doubtless begins at that point when the "drift" of crystals reaches its optimum height. Again,

¹ Kāgi: *Helv. Chim. Acta.* **6**, 264; *Kolloid-Z.*, **33**, 284 (1923).

² Davies: *J. Am. Chem. Soc.*, **44**, 2705 (1922); Davies, Taylor and Riblett: *J. Phys. Chem.*, **34**, 842 (1930).

³ Alexéeff: *loc. cit.*; Fischer-Treuenfeld: *loc. cit.*; Köhler: *loc. cit.*; Vorländer and Ernst: *loc. cit.*; Hughes: *loc. cit.*; Schubnikov and Lämmlein: *Z. Krist.*, **67**, 329 (1928).

the necessity of an air interface is understood on this theory, since this factor permits of the free movement of the melt, which is so vital a condition.

The theory of Vorländer and Ernst is insufficient, however, for it does not take into account the effect of the latent heat of crystallisation, and hence supplies no explanation of the influence of supercooling.

It would be anticipated that the crystallisation of a nucleus would continue with increasing height until the capillary force between the crystals and the melt had been balanced by the opposing capillary force exerted between the slide and the melt, whereupon crystallisation would proceed in continuous fashion at that limiting height. If, however, the melt in the close vicinity of the crystals increased in temperature, in virtue of the latent heat of crystallisation, the surface tension between the crystals and the melt would diminish and so disturb the balance between the two capillary forces in equilibrium. The melt would consequently descend from the crystal network. This would conclude the growth of the first "drift," and the second "drift" would begin its growth from the base of the first.

This effect of the latent heat of crystallisation would be possible only in a supercooled melt, since this condition permits of crystallisation with increasing temperature of the melt. If the melt were not supercooled, crystallisation would proceed without any fluctuation of temperature. Therefore, it follows that non-supercooled melts should crystallise in continuous fashion, whilst in the supercooled state melts may crystallise rhythmically.

It is interesting to note that the apparent rhythmic crystallisation of myristic, lauric, undecic and decic acids investigated by Garner and Randall¹ was ascribed to the formation of a solid skin which wrinkled and gave a waved effect upon the surface of the melt. This feature is distinct from the phenomenon discussed in this paper.

The general equation, $\log N = a \log r + \log K$, suggested by Hughes,² relating the number of bands (N) with the distance from the nucleus (r), has been borne out reasonably well in a number of instances of measurements made upon rhythmic bands of 3:5-dichloro-4-methyldiphenyl.

It is remarkable that rhythmic crystallisation of melts is confined to certain particular substances which have nothing in common with regard to their molecular structures. They are representative of many classes of compounds, and generally possess more or less powerful polar groups. Some have symmetrical formulae, others have not. Furthermore, only a few possess particularly long molecular structures.

The physical factors contributing to the phenomenon have still to be more fully understood. Doubtless, they include all the factors considered in this paper, and it is hoped to carry out soon a more quantitative study of them.

Summary

1. Rhythmic crystallisation of thin films of molten piperonal, terpin hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol and 3:5-dichloro-4-methyldiphenyl has been observed.

¹ Garner and Randall: loc. cit.

² Hughes: loc. cit.

2. Investigations upon the effects of supercooling, the presence of an air-interface and the thickness of film have been made upon 3:5-dichloro-4-methyldiphenyl. It has been shown that these factors control the production of rhythmic crystallisation.

3. The details of rhythmic growth have been observed upon a lantern screen by means of an epidiascope, using melts of 3:5-dichloro-4-methyldiphenyl, salol and piperonal.

4. By modifying and amplifying the theory of Vorländer and Ernst, it is possible to supply a satisfactory explanation of rhythmic crystallisation and the factors governing it.

The author wishes to express his thanks to Mr. G. J. Strickson, A.R.P.S., of this College, for the help he rendered in procuring the photographs and photomicrographs, and also to Messrs Imperial Chemical Industries for a grant made to this Department.

*Chemistry Department,
The Technical College,
Cardiff.
March 24, 1932.*

NOTE

BY STUART MUDD AND R. L. NUGENT

Reiner and Fischer¹ in 1929 developed a formula for the change in free energy incident to altered dispersion of a microheterogeneous system. Mudd, Nugent and Bullock² subsequently reached a similar formula from somewhat different considerations. The two formulae are essentially equivalent except for differences in notation. However, we criticized adversely (p. 243) the derivation of the formula of Reiner and Fischer on the ground that they introduced expressions for the free surface energies of the disperse phase and of the dispersing medium whereas the only free energies actually in question are the interfacial energies. We did not understand at the time that the two first-mentioned free surface energies were introduced as factors in a reversible step in the derivation of the total free energy change. This fact has since been brought to our attention by Dr. Reiner. We regret that this misunderstanding should have occurred on our part, and wish to emphasize that we fully realize that the treatment of Reiner and Fischer involves the understanding that, in the ideal reversible case, the total free energy change involved in an increase in interface in a microheterogeneous system is given by the product of the increase in interfacial area multiplied by the free interfacial energy per unit area.

We further stated that certain measurements of Harkins, Clark and Roberts show that the difference between the work of cohesion of a substance and its work of adhesion with a second substance is not equal to the interfacial tension between the two. This statement is correct, but does not concern the treatment of Reiner and Fischer, because their derivation involves the sum of the works of cohesion of the particles and of the dispersion medium rather than the work of cohesion of the particles alone.

University of Pennsylvania.

¹ Z. Immunitätsforschung, **61**, 320 (1929).

² J. Phys. Chem., **36**, 239 (1932).

NEW BOOKS

Vision and Colour Vision. By R. A. Houston. 22 × 14 cm; pp. iv + 238. London: Longmans, Green and Co., 1932. Price: 15 shillings. Dr. Houston's valuable researches on vision presaged a volume on the subject of more than common interest, and those who, knowing his flair for exposition, looked forward to a clear, orderly and fully documented account of the subject, have found their expectations realised, although on occasion they could wish that he had made more critical use of the information collected. To give in detail the subjects handled by Dr. Houston would reduce this review to a catalogue; stated as briefly as may be, they concern the discrimination of intensity, dark adaptation, acuity, the visibility of the spectrum, colour mixing, recurrent vision and flicker, fatigue, and simultaneous contrast and spatial induction. These topics account for three-quarters of the book; the remaining sixty pages give a detailed discussion of theories of colour vision and of the results of the examination of some two dozen colour blind subjects, collected from a student population of about a thousand. As was to be expected, Dr. Houston has not been content, apart from his own experiments, to take his knowledge at second hand; and much of the value of the work lies in its careful analyses of, and references to the original sources.

To the reader whose interests are not over-specialised there are two outstanding topics of special interest handled by the author. The first refers to the much discussed question of the Weber-Fechner law. Stated bluntly and without certain necessary reservations, sensation is proportional to the logarithm of the stimulus. Now, stimuli are physical quantities measured in terms of physical magnitudes. A pressure, a brightness (measured in millilamberts) the intensity of a sound (measured in micro-watts per square centimetre) are all definite objective physical stimuli. And if sensations are proportional (within a certain region) to the logarithms of these stimuli, we have at hand an algorithm which makes it possible to calculate the magnitude of a sensation. "Can't be done," say some physicists, some physiologists, and a great many psychologists. Why not? The answers vary in value and in clearness, but the fundamental fact on which most of them are based is that the process of measurement consists in laying alongside the magnitude to be measured another magnitude of the same kind (termed the unit) and finding how many times the unit can be stepped off along the magnitude to be measured. "Where is your unit of sensation?" ask some critics. "Is it ever possible to regard a sensation as built up of elementary magnitude?" ask others. Attempts to answer these queries were made by formulating a scheme of measurement which concerned itself with the determination of the *interval* between two sensation-magnitudes rather than with that of the magnitudes themselves. Titchener, among the greatest of the experimental psychologists, puts the matter perfectly clearly, though he is not to be regarded as the originator of the doctrine. He shews that a *scale* of sensation can be laid off— as a particular instance he describes a well-known experiment in which, by appeal to visual sensations alone, a series of grey papers of different shades are arranged in equal steps of increasing brightness. A photometric comparison of the objective brightnesses of these papers then shews that the brightnesses increase in a geometrical progression. The Weber-Fechner law may then be deduced in the form

$$S_1 - S_2 = k \log (I_1/I_2) \quad (1),$$

where $S_1 - S_2$ is interpreted as a sense-interval. Hence, just as the height of a vertical pole may be determined in terms of the foot, so may the *interval* between two sensations be measured. But any one sensation is a point on a scale, and can no more be measured, in *itself*, than can the top of the pole, which, in itself, is merely a point on a scale of heights.

Thus for Titchener; Dr. Houston adopts a method which may be interpreted in similar terms. He shews, for example, that a scale of brightness sensations may be built up by means of a simple experiment with a wedge photometer. Two lamps, A and B, are adjusted in position until the two faces of the photometer are equally bright. Readings of the posi-

tions of A and B are taken, and A is moved in until one face of the wedge is just noticeably brighter than the other. B is moved in until balance is just restored, then A is again moved in, and so on. Taking these steps as measures of unit sensation distance, experiments are described which shew how steps of different magnitude may be taken along this scale. He adopts, also, another method of description, and it is a matter for discussion whether the two methods are, or are not, fundamentally identical.

Consider, for a moment, the ordinary statement of *Weber's law* (not the Weber-Fechner law) which, we must remember, is an experimental law, and is concerned purely with objective stimuli. If the magnitude of any stimulus is I , then the least perceptible increase (δI) of the stimulus, is proportional to that stimulus. Thus, if an observer can just distinguish between the weight of 29 and of 30 *drams*, he will just be able to distinguish between 29 and 30 *ounces*. As usually stated,

$$\delta I/I = k.$$

The method of statement is unfortunate, and a certain amount of confusion has arisen from the occasional non-recognition of the fact that δI is not a differential, but is a differential coefficient. It is the rate of increase of stimulus with sensation, and should be written ($\delta I/\delta S$). The statement of the law is now ($\delta I/\delta S$) = kI , and in this form may be taken as unexceptionable. But if we integrate to obtain

$$S = k \log I + C, \quad (2)$$

we are tacitly assuming that $\sum \delta S = S$, that is, that a sensation may be regarded as built up from a number of elements of sensation—a conclusion which is hotly contested in many quarters.

In spite of Titchener's distinction between "distance" measurements and absolute determinations of sensation-magnitudes, it is questionable whether his argument (which is the argument of most psychologists since Delboeuf) does more than evade the point; equation (1) is of course a direct deduction from equation (2), and *any* formulation of the Weber-Fechner law involves, tacitly or overtly, an integration of the Weber equation and the consequent assumption that $\sum \delta S = S$. The fact is, that experimental psychologists in the main have been obsessed by the picture afforded of length-magnitudes built up by the direct opposition of unit-lengths, and that of sensations as points on a scale of "distances." Stumpf's observation "Jede Empfindung präsentiert sich als Unteilbares" has been the theme of volumes of criticism all tending to shew that it is the "sensation-interval and not the sensation itself that is measured, all based on the length-analogy just described. And yet, if we break away from the dominating length-analogy, a magnitude such as the surface-tension (T) of water at 15°C "präsentirt sich als Unteilbares," a fact which does not in the least dismay us, when, faced with an equation such as $dT/d\Theta = f(\Theta)$, we integrate and obtain a consistent and correct delineation of the variation of surface tension with temperature.

Again, a certain weight of criticism has been brought to bear on the assumption, commonly made, that the just noticeable differences on which a scale of sensation has been built up (compare Dr. Houston's wedge-photometer experiment, just cited) are *equal* unit-steps on the scale of sensation. Many of the criticisms are of very doubtful validity; thus, Fechner maintained that the just noticeable difference of sensation obtained when one dram is added to twenty-nine drams is equal to that obtained when one ounce is added to twenty-nine ounces. It has been seriously advanced as a criticism of this attitude that, were this so, an ounce and a dram would produce an equal sensation—as remarkable an *ignoratio elenchi* as has ever come before the writer's notice.

Dr. Houston does not spend much time in considering critically the dicta of adverse commentation in this field; he remarks, in effect, *solvitur ambulando*, and proceeds, unperturbed, with his investigations—an attitude towards which the present reviewer confesses a certain amount of sympathy. Adopting, then, the possibility of putting $\sum \delta S$ equal to S , Dr. Houston, in the matter of visual intensities, has made a very notable contribution to knowledge by plotting $I \times (\delta I/\delta S)$ as ordinate against $\log I$ as abscissa. It will be seen that an element of area $y \, dx$ under the resulting curve is

$$(I\delta S/\delta I) \times \delta(\log I) = \delta S,$$

so that "the sensation at any point on the axis of abscissae is proportional to the area to the left of that point. This holds no matter what the shape of the curve is."

Further, the experimental points fit, with considerable accuracy, a Gaussian probability curve, so that for any value x ($= \log I$) of the abscissa, the sensation corresponding to the intensity I is given by

$$S = \int_{-\infty}^x 1 - 1/x^2 - dx.$$

One minor point may be noted. In a work making great use of a measure of sensation the very existence of which is in dispute, it is necessary to be meticulously careful in matters of nomenclature. Dr. Houston (p.2) discusses a "unit of the sensation of brightness" which "is wholly subjective." This is the quantity which we have been discussing at some length. A little later (pp. 8 and 9) he writes of the measurement of "subjective brightness, the brightness of the image on the retina," and points out that "when the brightness of the object is m milli-lamberts and the area of the pupil is a square millimetres, the brightness of the image on the retina is said to be ma " units. This last-named unit is obviously purely objective, and the double use of the term *subjective* is unfortunate.

Dr. Houston's book, whether regarded as a compendium of standard knowledge, or as a comprehensive account of recent investigations, is an important contribution to existing literature. Beginners in the subject may have to tread warily when reading certain sections, but the advanced student will find the book everywhere stimulating and suggestive.

Allan Ferguson

Das ultrarote Spektrum. By Clemens Schaefer and Frank Matossi 22 × 14 cm. pp. vi + 400. Berlin: Julius Springer, 1930. This is the tenth volume of the "Struktur der Materie" series of monographs edited by Born and Franck. The experience of the authors, gained by original work in the field of infra red radiation, has enabled them to produce a book which should be of value to two classes of readers; those who wish only a general survey of the field, for which purpose the book is complete in itself, and the research workers in this field for whom the very complete list of references will be useful in seeking the details of the experiments in which they may be interested.

The authors have, for the most part, treated only those phenomena in which infra red radiation plays the main rôle. They have, accordingly, left out all accounts of phenomena in which electronic transitions occur, either alone or in conjunction with other energy changes in the molecule. There is a very good interweaving of theoretical discussions and descriptions of the experimental work which makes the book very readable. Although the main part of the book is taken up with the more modern aspects of research in the field, a brief account of the older work is included to make the book a fairly complete account of the subject to date.

After a brief historical introduction, the first chapter is devoted to a discussion of the various experimental methods employed in the investigations. The second chapter is a very brief discussion of the theoretical and experimental work on thermal radiation. The third chapter is an account of the Maxwell theory of radiation and its application to the optical properties of insulators and metals.

The fourth and fifth chapters form the main part of the book and, indeed, are the justification for the appearance of the volume. The fourth chapter contains a discussion of the modern theory of band spectra due to transitions in molecular states in which there is no electronic transition. The application of the theory to the problems of molecular structure and dissociation energies is pointed out. In addition to this discussion of problems associated with spectra from free molecules some space is given to the absorption spectra of liquids. The fifth chapter contains a treatment of the Born theory of crystal vibration and its application to the infra red spectrum of crystals. A great deal of experimental work in this field is described and the bearing of the theory on the results pointed out. These last two chapters contain a very good résumé of the recent work and on this account the book will be indispensable in the research laboratory.

J. R. Collins

Colloid Chemistry. Edited by Jerome Alexander. Vol. IV. 23 × 16 cm; pp. 734. Chemical Catalog Company, 1932. Price: \$11.50. This volume is the second covering technological applications. The subjects discussed are: carbohydrates, including cellulose, wood, paper, explosives, sugar, starch products, sizing; dyeing; rubber, including latex and carbon black; plastics; tanning; photography; coatings, including paints, color lakes, and electrodeposition; foods; laundry and dry-cleaning; solidified alcohol and fire extinguishers; water supply and sewage disposal.

The papers and authors are: colloid chemistry of cellulose, Max Samec; colloid chemistry of wood and wood-formation, H. Wislicenus; colloid chemistry in the paper industry, R. Lorenz; cellulose esters, E. W. J. Mardles; smokeless powder, C. G. Storm; structural variations in smokeless powders, A. J. Phillips; colloid chemistry in the sugar industry, R. I. Balch and H. S. Paine; applied colloid chemistry in confectionery manufacture, Stroud Jordan; a summary of the colloid chemistry of starches, Max Samec; starch and some of its derivatives, V. G. Bloede; sizing and finishing of textile materials, L. A. Olney; the process of dyeing, Georg Georgievics; dyeing, William Harrison; theory of dyeing, W. D. Bancroft; the colloid chemistry of rubber latex and its industrial applications, A. van Rossem; the structure of rubber, E. B. Spear; physico-chemical aspects of Hevea rubber, R. P. Dinsmore; carbon black in the rubber industry, N. A. Shepard; synthetic resins, H. L. Bender; dispergation and aggregation of natural silk in aqueous solutions of neutral salts, P. P. von Weimarn; technologically useful properties of casein, F. L. Browne; tanning, and the modern theory of colloidal swelling, H. R. Procter; tanning, E. Stiasny; tanning, G. D. McLaughlin; colloid chemistry and photography, Lüppe-Cramer; colloids and photochemistry, S. E. Sheppard; color photography, H. Mouquin; notes on colloidal phenomena in paint and varnish products, H. A. Gardner; colloidal aspects of paint and varnish removers, Norris Boehmer; water-Japan, W. P. Dewey; synthetic mother-of-pearl, L. Clément and C. Rivière; color lakes, H. B. Weiser; addition agents in electrodeposition, William Blum; colloidal aspects of baking chemistry, C. N. Frey and Quick Landis; butter and margarine from the standpoint of colloid chemistry, William Clayton; colloidal chemistry and the art of brewing, Fritz Emslander; the pectic substances, Ruth Johnston and Mary A. Griggs; "solidified" alcohol, P. C. L. Thorne and C. G. Smith; alkaline and other detergents, H. G. Elledge; the colloid chemistry of washing, L. Zakarias; the foam method of extinguishing fire, C. B. White; colloidal aspects of waste treatment, A. M. Buswell.

"Sugar is adsorbed by cellulose from alcoholic solution, a circumstance which can cause large errors in the determination of sugar in beets by alcoholic digestion," p. 14. The salts of organic bases are adsorbed by cellulose both in neutral solution and in a solution containing soda; in some cases the addition has a favorable influence, in other cases an arresting influence, on the adsorption. The strong adsorption of diamine salts (except o-phenylene diamine), benzidine, and the hydrazines is remarkable," p. 18. "Schwalbe attained the maximum swelling of cellulose by beating in a 0.1 percent solution of lactic acid; cellulose fibers impregnated with such a liquor retain five times their own weight of water after being centrifuged, whereas cellulose swelled in water alone does not bind more than one and a half times its own weight of water," p. 78.

"Traube found that latex will cream at a temperature of 50° after the addition of mucilaginous substances, such as a two percent sol of Irish moss. It has long been known that creaming of ordinary cow's milk is accelerated considerably by the addition of such substances; but this process is carried out in the milk industry at a low temperature, about 10°. Some experiments carried out at the Netherlands Government Rubber Institute with an ammoniated latex showed that the creaming of rubber latex is successful only at higher temperatures, e.g. 50°. Preliminary experiments proved albumin, casein, and gelatin to be ineffective; but, besides carrageen (Irish moss), tragacanth, saleb, agar-agar, and pectinous substances gave positive results," p. 257.

"When calcium carbonate is formed by diffusion into a colloidal mass, it automatically forms itself into an alveolar net-work, which optically, produces a pearly effect. Pearliness is not a specific property of calcium carbonate; in fact we can produce a more or less beauti-

ful pearly effect with other salts—barium, lead, silver, copper. The superior beauty of calcium carbonate pearl is due to its fineness of grain. . . . We believe that our experiments represent a true synthesis," p. 504. Unfortunately Clément and Rivière did not determine whether the calcium carbonate was precipitated as aragonite.

Some of the more important emulsifying agents and their uses as employed in the baking industry are: gelatin for icings; egg albumen for cakes and frostings; egg yolks for cakes and custards; Indian tragacanth (Karaya) for icings; stearines and oxidized vegetable oils for caramels; and lecithin for cream fillings, p. 560.

"A garment or other textile article ready for the laundry or for dry cleaning is said to be soiled, a term really including dirty and stained. Loosely the three expressions are used synonymously. There is some precedent in the limited writings on cleansing to use the word stain to designate the more refractory localized discolorations, and dirt the more common soiling bodies. In these senses they are used here. Dirt is simply adsorbed particles, discolorants left on a surface by contact or by evaporation of a dispersing fluid. A stain usually requires treatment other than that accorded in the regular cleansing procedure. Thus in ordinary water washing, chewing gum is a stain, because it is most readily removed by a special solvent, namely carbon tetrachloride. In dry cleaning, maple syrup is a stain, because waterborne stains are not removed by the usual petroleum solvent," p. 636.

Wilder D. Bancroft

Introduction to Agricultural Biochemistry. By R. A. Dutcher and D. E. Haley. 23 × 15 cm; pp. ix + 484. New York: John Wiley and Sons, 1932. Price: \$4.50. "The present volume is an outgrowth of lectures presented to agricultural students over a period of nearly twenty years. The book is designed for those students who have had preliminary training in inorganic and organic chemistry," p. v. It represents a well-written, interesting, and teachable survey of a large number of fields related to the interests of agricultural students. The book is divided into three parts.

Part one deals with the general applications of chemistry to these fields, and includes chapters on the development of agricultural chemistry, the chemistry of living matter, the carbohydrates, fats and related compounds, proteins, enzymes, and a chapter on the physical state of matter which includes a brief discussion of certain phases of colloid chemistry which are recognized as of dominant importance.

The second part is concerned with the plant, with especial emphasis on the plant food. This includes chapters on seed germination, the soil, soil acidity, farm manure, fertilizers, the atmosphere, insecticide and fungicides and related materials, absorption of mineral nutriment by plants, assimilation of mineral nutriment by plants, the plant carbohydrates, plant lipoids, vegetable proteins and related compounds, and respiration.

In the third part the animal is discussed in chapters entitled: foods and feeding stuffs, digestion of food, body tissues, metabolic changes in tissues, energy metabolism, biological response to foods, protein quality, vitamin A, vitamin B complex (B and G), vitamin C, vitamin D and ultraviolet light, and vitamin E. The chapters on nutrition and on the vitamins are particularly interesting and include much of the work done by the senior author in that field.

Throughout the book the writing is done in such a manner as to stimulate the reader to refer to some of the general references given at the end of each chapter. The impression is conveyed that the application of chemistry to many of these biochemical problems is but well begun and frequent are the points which are still in doubt. For these, condensed statements are given of the evidence now in and a basis laid for the correlation of the evidence yet to come.

The general philosophy which appears to underlie the book is refreshing. In the first chapter, after describing the experiment of van Helmont in which he believed he had grown one hundred sixty-four pounds of wood, bark, and roots of his willow tree from water alone, the authors comment; "This experiment, however, is thoroughly typical of much of the early investigational work in agricultural chemistry, as well as of other sciences. In this, as in

other branches of science, it is very easy to fail to consider a vital factor and as a result, draw, from perfectly good experiments, a conclusion which appears to be correct but which is, in reality, entirely wrong. In the work cited above, van Helmont failed to take into consideration two most important factors, namely, the rôle played by the constituents of the atmosphere and the two ounces of soil which had disappeared. Hopkins has very truthfully said that an experiment is a question put to Nature, and Nature always answers every question truthfully, but the question that Nature answers and that the experimenter asks is not always the question that he thinks he asks," p. 7.

This book has many features to commend it and should prove an effective textbook for courses in agricultural biochemistry.

Herbert L. Davis

Das periodische System in neuer Anordnung. By Darwin O. Lyon. *Second edition.* 26 × 18 cm; pp. 40. Leipzig and Wien: Franz Deuticke, 1931. Price: 8 marks. This book is essentially a work of reference on the physical properties of the chemical elements. These are presented to the reader in many tables, spirals and charts, some of which are in the form of those slight departures from the conventional, best representations of the periodic classification, which every writer on the subject feels actuated to make. These novel features were described and discussed, and, on the whole, commended in these pages (32, 1891 (1928)), at the time of publication of the original edition. The merit of the present work is that the great mass of information on many physical properties of the elements has been brought up to date. To those who did not see the first edition it may be said that Dr. Lyon's book is a breakaway from a survey of the periodic classification to which chemists are accustomed: from the chemical or physical-chemical points associated with such names as Mendeléef, Bohr and Aston. The author is concerned almost exclusively with the periodicity of such physical properties as magnetism (of which he has evidently made a special study, and on which he is good), resistance, entropy, thermal expansion, and sound conductivity, as well as the more usual properties which the textbooks describe. Nothing very novel has emerged in these compilations, but the information has been carefully collected and is critically as well as strikingly represented. The book is not in any bad sense 'viewy'. It is a work of learning which might well be included in a physical chemist's library.

A. S. Russell

Kapillarchemie. *Eine Darstellung der Chemie der Kolloide und verwandter Gebiete.* By Herbert Freundlich. *Fourth Edition, revised with the assistance of J. Bikerman.* Vol. I. 24 × 18 cm; pp. viii + 566. Leipzig: Akademische Verlagsgesellschaft, 1930. Price: 36 marks, bound 39 marks. The fourth edition of this standard work is issued in two volumes. The first volume includes a discussion of the fundamental physical-chemical principles of colloid chemistry which the author groups under the term Kapillarchemie.

The book is divided into three portions, the first of these filling about 90% of the book under the general title Kapillarchemie. Discussion of the phenomena at various types of interfaces is the outline. These include liquid-vapor, liquid-liquid, solid-vapor, and solid-liquid. The first division also includes chapters on electrical phenomena and the properties of interfacial layers. The second division of the book treats of the kinetics of the formation of a new phase, particularly of a new solid phase. In the third division is found a discussion of Brownian movement and its mathematical formulation and significance.

From the standpoint of economy as well as that of convenience of use, it seems that a single volume edition might have been preferable even if it meant some omissions or abbreviations of discussion. The new edition is, like the previous ones, fitted to take a high place as one of the best reference books for workers in colloid chemistry. Revision has been extensive and the book represents a valuable survey of the phenomena illumined by the interpretations of a master of this fast-growing field.

Herbert L. Davis

SEDIMENTATION OF CLAYS¹

BY E. W. KANNING, R. J. HARTMAN AND FLOYD CHILDS

Introduction

The rate of sedimentation of particles from aqueous suspensions is a measure of the particle size. This was first shown by Stokes² in his classical discussion in the year 1846.

The combined forces which start any motion in suspended particles are due either to the buoyant force of the liquid or to the force of gravity. The force of gravity is always downward and is constant at a given location under similar conditions. As soon as the suspended particles start to fall, the retarding force of the liquid becomes active. This force is due to the viscosity of the liquid and is equal to $6\pi nr v$ where n is the viscosity coefficient of the liquid, r is the radius of the particles, and v is the velocity of settling in centimeters per second (constant rate of fall). This retarding force acts in opposition to gravity which is equal to $\frac{4}{3}\pi r^3(d_1 - d_2)g$. Where d_1 is the specific gravity of the particles, d_2 is the specific gravity of the liquid, and g is the gravitational constant expressed in dynes. If the retarding force due to the viscosity of the liquid is equal to the force of gravity, the rate of settling of the particles would be constant. This may be shown by

$$6\pi nr v = \frac{4}{3}\pi r^3(d_1 - d_2)g.$$

From this equation is derived Stokes' law

$$v = \frac{2r^2(d_1 - d_2)g}{9n}$$

In any specific instance where the same material is suspended, d_1 , d_2 , g , and n are constant, and, therefore, the equation may be written

$$v = Kr^2 \quad \text{or} \quad r^2 = v/K.$$

Where particles are so small that sedimentation does not take place Stokes' law does not apply, since other forces such as Brownian movements act to keep the particles in suspension.

In this investigation Stokes' law has been applied to dilute aqueous clay suspensions for the measurement of the size and the velocity of fall of the particles. The clays studied are representative samples⁴ from nine entirely different clay deposits in the state of Indiana.

¹ Contribution from the Laboratory of Colloid Chemistry, Indiana University, Bloomington.

² Phil. Mag., 29, 60-62 (1846); Camb. Phil. Soc. Trans., 8, 287-319 (1846); 9, 8 (1856).

³ "Mathematical and Physical Papers," 3, 1 (1910). For modifications and limitations see Cunningham: Proc. Roy. Soc., 83R, 357 (1910); J. Am. Chem. Soc., 41, 319 (1919); Millikan: Physik. Z., 11, 1097 (1910); Phys. Rev., (2) 22, 1 (1923); Ishida: Phys. Rev., (2) 21, 550 (1923).

⁴ These samples were collected and classified by George I. Whitlatch under the direction of Dr. W. N. Logan, state geologist and professor of geology, Indiana University.

Experimental

Clays studied: The various clays studied, their geologic classification and location from which they were collected are cited in Table I.

TABLE I

Clay No.	Geologic Classification	Geographic Location
1	Borden Shale	Brooklyn, Indiana
2	Pennsylvanian Under Clay	Ashboro, Indiana South Pit of Big Ben Coal Co.
3	Pennsylvanian Shale (Ruby Shale)	Evansville, Indiana Standard Brick Co.
4	Chester Shale	Huron, Indiana
5	New Albany Clay	Wolcottville, Indiana
6	Alluvial Clay	Evansville, Indiana Standard Brick Co.
7	Kaolin	Lawrence County, Indiana
8	Mahogany Clay	Willow Valley Lawrence County, Indiana
9	Glacial Residual	Fort Wayne, Indiana Fort Wayne Brick Co.

The clays were dried in air at room temperature for four months, and ground in a mortar until the entire sample passed through a 40 mesh sieve. The ground clays were quartered down to 50 gram samples from which an aliquot part was weighed for the study of sedimentation. The clay suspensions consisted of known weights of approximately five grams of dry clay dispersed in 200 cubic centimeters of pure distilled water.

Apparatus and Procedure: An apparatus for the determination of sedimentation such as that of Calbeck and Harner¹ was not available, therefore a modification of this apparatus was improvised. Fig. 1 illustrates the construction of the apparatus used for determining sedimentation in this investigation.

A—Beam of analytical balance.

B—Glass cylinder, 10.16 cm. tall and 6.98 cm. diameter (inside measurements), resting on the bridge D.

C—Balance pan.

D—Wooden bridge over balance pan clearing same 2 cm.

E—Thin copper disc, 4.2 cm. in diameter.

F—Copper wires soldered to the disc E at three equidistant points.

G—Cork stopper.

H—Aqueous clay suspension.

I—Floor of balance.

J—Thermometer suspended from balance case.

J. C. Ware: "Chemistry of the Colloidal State," 36 (1930).

Into the glass cylinder B was placed 200 cm. of pure distilled water at 20°C. measured accurately with a pipette. This volume covered the copper disc E with 5.1 cm. of water. Approximately 35.32% of the total volume of the liquid was above the copper disc. The disc was tared by placing sufficient weights on the opposite pan. Approximately five grams of dry clay accurately weighed was added to the water and the mixture vigorously agitated by means of the copper disc E, temporarily disengaged from the balance hook. When the clay particles were thoroughly dispersed in the water the agitation was stopped, the copper plate replaced and a stop watch

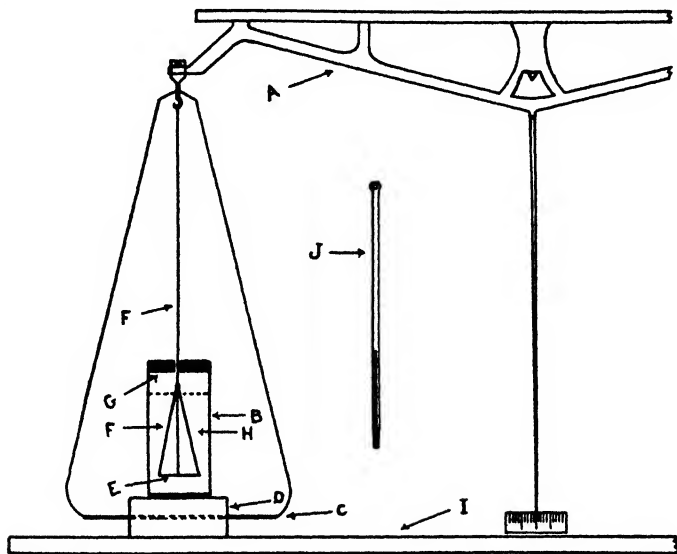


FIG. 1

started. The balance arrest was adjusted so that the beam could swing only through a very small angle, causing a deflection of the pointer on the scale of but one division in either direction. As the clay particles settled on the disc E the pointer began to swing to the right. During the period of sedimentation it was necessary to add weights to the right pan and adjust the rider on the balance beam so that when a definite time period expired, the exact weight of the clay particles on the disc could be recorded.

The same apparatus was applied to the determination of the specific gravity of the dry clays. The specific gravity was found by dividing the weight of the dry clay by the loss of weight in water. In order to determine the weight of the clay in water, a small porcelain crucible was placed on the disc E, immersed in 200 cc. of distilled water in the glass cylinder B, and weighed. The disc was lifted and nearly all of the water poured out of the crucible back into the vessel and a known weight of clay placed in the crucible. Sufficient time was allowed for the clay to be thoroughly wetted by the water in the crucible. The crucible was then very slowly submerged in the water to prevent washing any of the clay sample out of the crucible. (This opera-

tion required several minutes). The weight in water of the crucible and clay was taken and the weight of the clay in water calculated by difference. The loss of weight in water was obtained by subtracting the weight of the clay in water from the weight in air.

Data and Results: Table II gives the specific gravity of each clay as determined in the above described manner.

TABLE II
Specific Gravity of Clay Samples

Clay No.	1	2	3	4	5	6	7	8	9
Specific Gravity*	2.53	2.40	2.53	2.51	2.43	2.90	2.26	2.45	2.41

* Each clay sample contained particles of various specific gravities; therefore, the specific gravity as determined is a mean value for all particles in that sample.

In order to determine the radius of the particles of clay samples it was necessary to determine by calculation the velocity of fall of particles (v in Stokes' law) settling at the definite experimental time intervals. The velocity in cm. per second was determined by dividing the distance of fall (5.1 cm.) by the total time elapsed in seconds for each time interval. Table III shows the velocity of fall of the clay particles settled out at definite indicated time intervals from aqueous suspension.

TABLE III
Velocity of Fall of Clay Suspensions in Water

Time in min. to fall 5.1 cm.	Time in sec. to fall 1 cm.	Velocity in cm. per second	Time in min. to fall 5.1 cm.	Time in sec. to fall 1 cm.	Velocity in cm. per second
2	23.53	.042500000	45	529.38	.001888888
5	58.82	.017000000	60	705.84	.001416666
10	117.64	.008500000	75	872.30	.001133333
15	176.46	.005666666	90	1058.76	.000944444
30	352.92	.002833333	120	1411.68	.000708333

Stokes' law was applied in determining the radii of the various clay particles by using the specific gravities of the various clays given in Table II, the velocities in centimeters per second for the various time intervals employed in the experimentation (Table III), the specific gravity and the viscosity coefficient of water at 20°C., and the gravitational constant. Table IV shows the results, mathematically calculated from Stokes' law, of the radii of the particles of the various clays studied. The radii of the clay particles, having settled at the definite indicated times, are equal to or greater than the values given in the table. At the expiration of two minutes the radii of the particles are equal to or greater than that indicated in Table IV for that time and not greater than that which would pass through a 40 mesh sieve. At any definite time thereafter the radii of the particles are equal to

or greater than that indicated in Table IV for that time but not greater than the value indicated for the preceding time. For example, the particles in Clay No. 1 which settled out in 2 minutes had radii equal to or greater than .0011315 cm. Since the sample had passed through a 40 mesh sieve, no particle larger than the apertures of the sieve could be present. There are unquestionably many particles whose radii will vary between these two limits and it is possible that during this first time period some particles even smaller than .0011315 cm. could have settled. These smaller particles may have settled from only a short distance above the disc. The radii of the particles of Clay No. 1 which settled out during the next 3 minutes (time = 5 min.) will be equal to or greater than .0007156 cm. and not greater than .0011315 cm. The same is true between any of the time intervals in Table IV.

TABLE IV
Radii in Cm. of Clay Particles*

Time in min. to fall 5.1 cm.	Number of Clay				
	1	2	3	4	5
2	.0011315	.0011821	.0011315	.0011523	.0011703
5	.0007156	.0007481	.0007156	.0007205	.0007402
10	.0005060	.0005290	.0005060	.0005093	.0005234
15	.0004131	.0004319	.0004131	.0004159	.0004273
30	.0002921	.0003054	.0002921	.0002940	.0003021
45	.0002385	.0002493	.0002385	.0002408	.0002467
60	.0002065	.0002159	.0002065	.0002079	.0002136
75	.0001832	.0001932	.0001832	.0001859	.0001911
90	.0001686	.0001763	.0001686	.0001702	.0001744
120	.0001460	.0001527	.0001460	.0001470	.0001510

Time in min. to fall 5.1 cm.	Number of Clay			
	6	7	8	9
2	.0010154	.0012467	.0011664	.0011731
5	.0006422	.0007885	.0007377	.0007419
10	.0004541	.0005566	.0005217	.0005246
15	.0003708	.0004552	.0004259	.0004283
30	.0002622	.0003219	.0003011	.0003028
45	.0002140	.0002628	.0002459	.0002473
60	.0001854	.0002276	.0002124	.0002141
75	.0001658	.0002036	.0001904	.0001915
90	.0001513	.0001858	.0001739	.0001748
120	.0001311	.0001609	.0001505	.0001514

* The radii of the various clay particles are equal to or greater than the value indicated for the various time intervals.

In order to determine the sedimentation curves for the clays with the procedure and apparatus previously described, it was necessary to obtain the data shown in Table V which includes the following: total time in minutes at intervals, total grams of clay particles settled at the indicated time inter-

vals, the increase in grams over the previous period which is the actual weight settled during each interval, the per cent settled of the total weight in suspension and the per cent settled between each interval. The per cent settled of the total weight in suspension was calculated with the total grams settled within the maximum time indicated at 100%. The per cent settled during each interval was calculated on the same basis.

TABLE V
Sedimentation of Clay Particles

Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per cent settled between each Interval
Clay No. 1				
2	.4278	.4728	62.4	62.40
5	.5367	.0639	70.9	8.45
10	.5834	.0467	77.0	6.16
15	.6099	.0265	80.5	3.50
30	.6446	.0347	85.1	4.58
45	.6651	.0205	87.8	2.71
60	.6746	.0095	89.2	1.25
75	.6833	.0085	90.9	1.12
90	.6894	.0061	91.7	0.81
120	.6988	.0091	92.9	1.20
1440	.7476	.0488	99.5	6.44
2880*	.7568	.0092	100.0	1.21
				Total 99.83
Clay No. 2				
2	.2500	.2500	43.3	43.3
5	.3282	.0782	56.9	13.5
10	.3802	.0520	65.9	9.0
15	.4113	.0311	71.3	5.4
30	.4605	.0492	79.8	8.8
45	.4831	.0226	83.7	3.9
60	.4912	.0081	84.6	1.4
75	.5008	.0096	86.8	1.6
90	.5092	.0084	88.2	1.4
120	.5201	.0109	90.1	1.9
150	.5283	.0082	91.1	1.4
1440	.5769	.0486	100.0	8.4
				Total 100.0

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

TABLE V (Continued)

Sedimentation of Clay Particles				
Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per Cent settled between each Interval
Clay No. 3				
2	.1493	.1493	32.1	32.1
5	.2294	.0801	49.3	17.2
10	.2900	.0606	62.3	13.0
15	.3100	.0200	66.6	4.3
30	.3618	.0518	77.2	11.1
45	.3772	.0154	81.1	3.3
60	.3890	.0118	83.6	2.7
75	.3980	.0090	85.5	1.9
90	.4042	.0062	86.6	1.3
120	.4100	.0058	88.1	1.2
150	.4151	.0051	89.2	1.1
1440*	.4653	.0502	100.0	10.8
Total				99.9
Clay No. 4				
2	.7699	.7699	94.7	94.700
5	.7977	.0278	98.0	3.410
10	.8017	.0040	98.4	0.490
15	.8053	.0036	98.9	0.440
30	.8054	.0001	99.0	0.001
45	.8055	.0001	99.0	0.001
60	.8063	.0008	99.1	0.009
75	.8071	.0008	99.1	0.009
90	.8080	.0009	99.2	0.011
120	.8097	.0007	99.3	0.008
150	.8106	.0009	99.5	0.011
1440	.8145	.0039	100.0	0.480
Total				99.570
Clay No. 5				
2	.4136	.4136	64.1	64.10
5	.4627	.0491	71.3	7.64
10	.4958	.0331	77.2	5.15
15	.5114	.0156	79.5	2.42
30	.5315	.0201	82.6	3.12
45	.5575	.0260	86.7	4.05
60	.5688	.0113	88.3	1.75
75	.5741	.0053	89.2	0.82
90	.5819	.0078	90.5	1.21
120	.5903	.0084	91.6	1.30
1440*	.6443	.0540	100.0	8.40
Total				99.96

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

TABLE V (Continued)
 Sedimentation of Clay Particles

Time in Minutes	Total Grams settled	Increase in Grams over Previous Period	Per Cent settled of Total in Suspension	Per Cent settled between each Interval
Clay No. 6				
2	.6443	.6443	64.8	64.80
5	.7655	.1212	77.1	11.32
10	.8359	.0704	84.1	7.13
15	.8581	.0222	86.5	2.21
30	.8993	.0412	89.6	4.15
45	.9184	.0211	92.4	2.11
60	.9293	.0109	93.6	1.15
75	.9350	.0057	94.3	0.57
90	.9429	.0079	95.0	0.79
120	.9517	.0108	95.9	1.14
2880*	.9945	.0428	100.0	4.33
				Total 99.80
Clay No. 7				
2	.3838	.3838	98.3	98.3
5	.3878	.0040	99.3	1.0
10	.3901	.0023	99.9	0.6
15	.3902	.0001	100.0	0.1
30	No gain	No gain	Total 100.0	
45	No gain	No gain		
Clay No. 8				
2	.6600	.6600	96.9	96.90
5	.6749	.0149	99.1	2.20
10	.6793	.0044	99.7	0.64
15	.6795	.0002	99.8	0.01
30	.6804	.0009	99.9	0.02
45	.6806	.0002	100.0	0.01
60	No gain	No gain	Total 99.78	
75	No gain	No gain		
Clay No. 9				
2	.5928	.5928	68.1	68.10
5	.6951	.1023	77.8	11.80
10	.7710	.0759	88.5	8.71
15	.7821	.0111	89.8	1.16
30	.8220	.0399	94.4	4.58
45	.8378	.0158	95.5	1.81
60	.8476	.0102	97.3	1.17
75	.8518	.0042	97.7	0.48
90	.8543	.0025	98.0	0.28
120	.8612	.0069	99.0	0.79
1440	.8712	.0100	100.0	1.15
				Total 100.03

* When the time indicated had elapsed the liquid above the disc was still very slightly turbid.

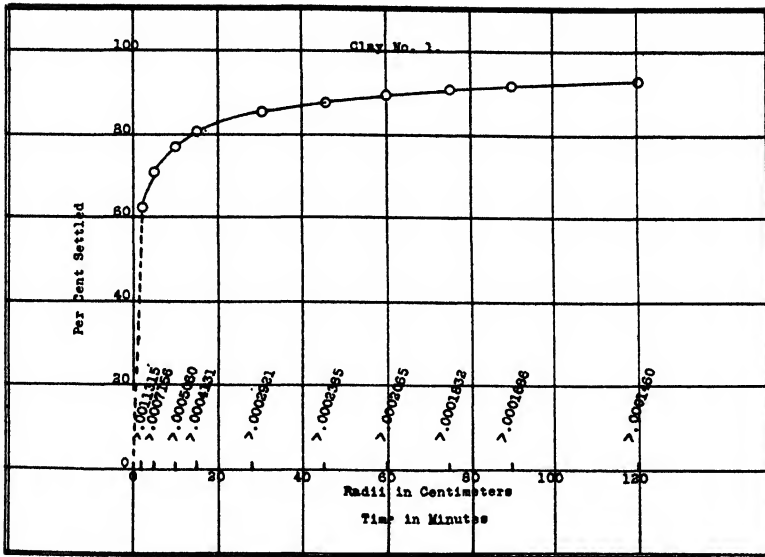


FIG. 2

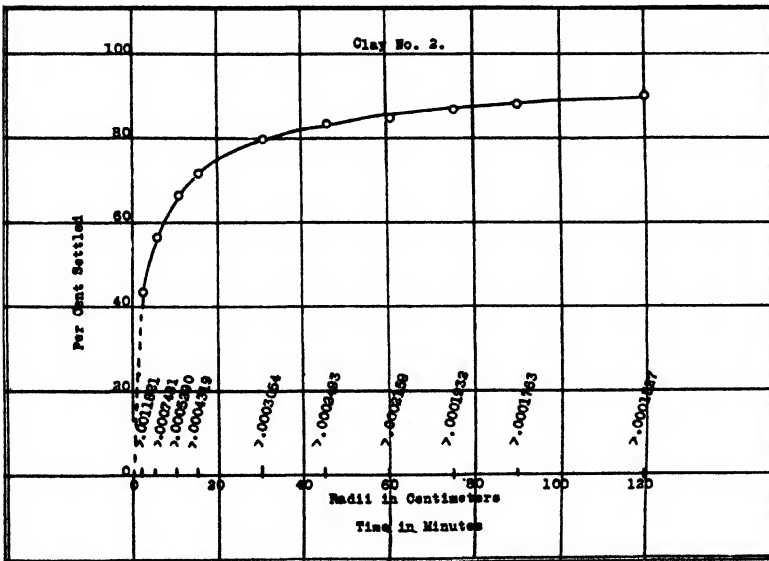


FIG. 3

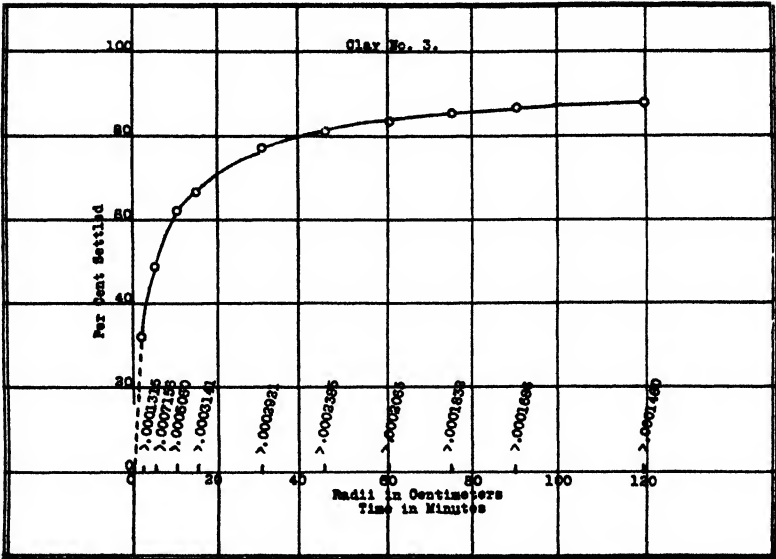


FIG. 4

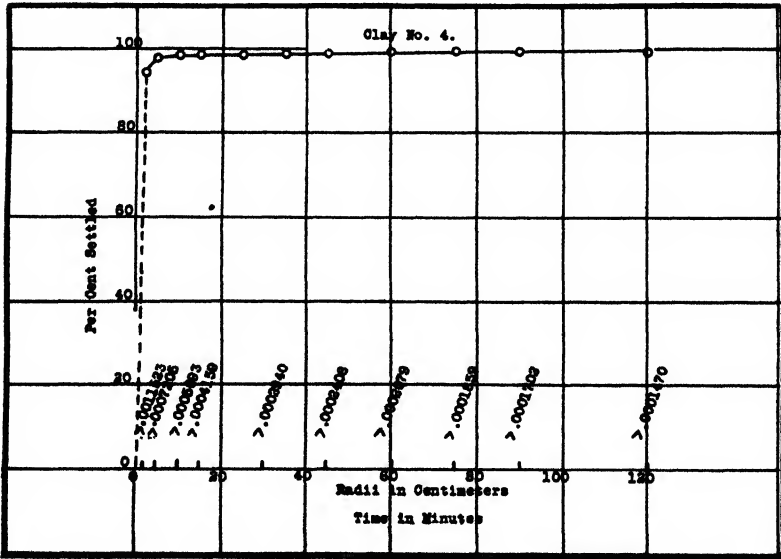


FIG. 5

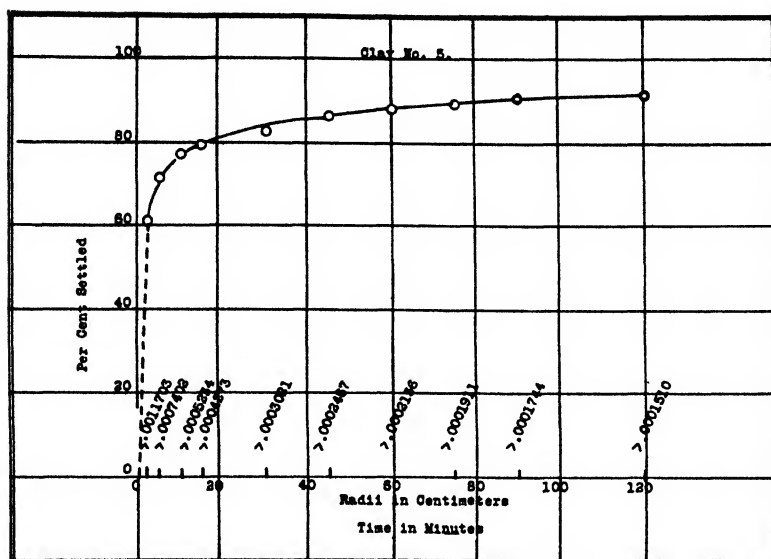


FIG. 6

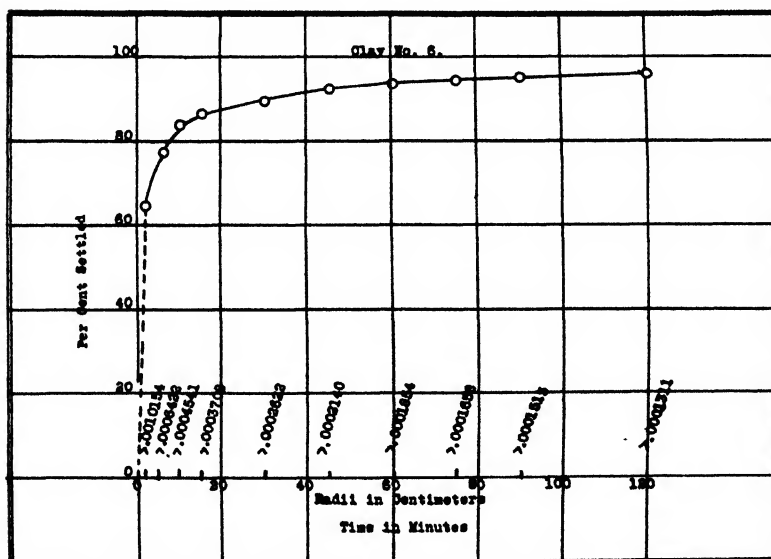


FIG. 7

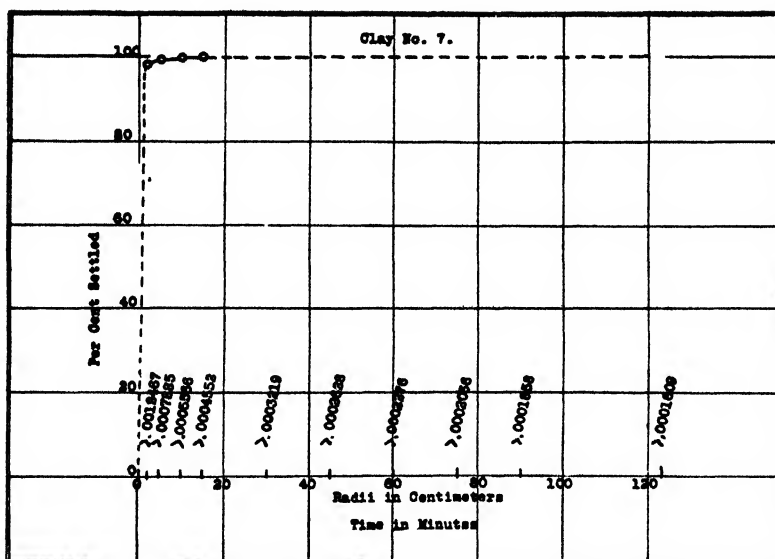


FIG. 8

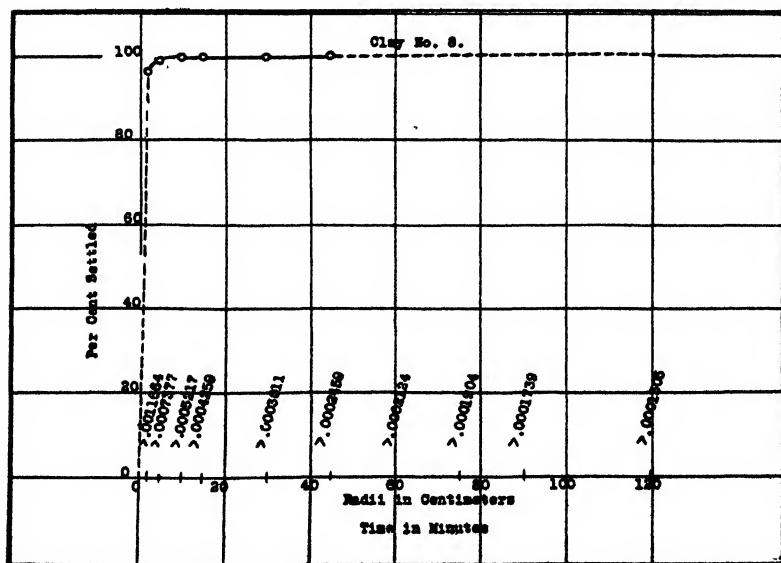
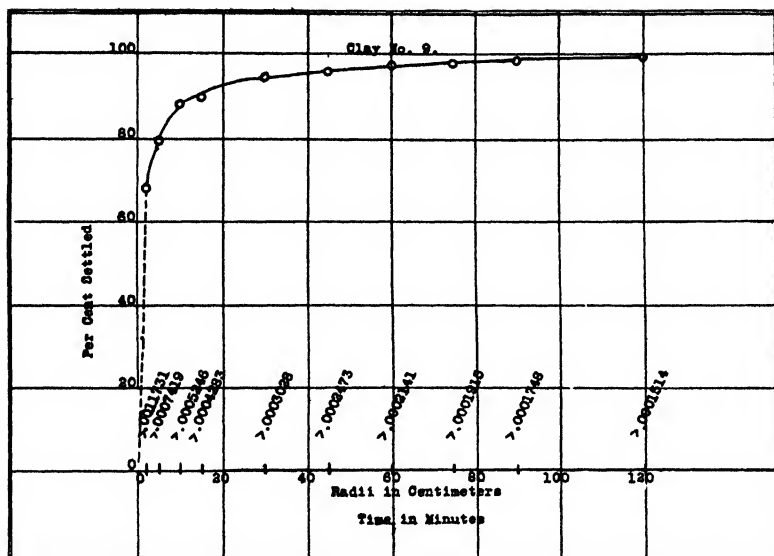


FIG. 9



the greatest mean specific gravity of any used in this investigation, did not settle out as rapidly as some of the others. This is evidently due to either one or both of two factors, first, the per cent of the smaller sized particles was greater and, second, the per cent of the particles having the lesser specific gravity was greater in comparison to the other clays studied.

It was also noted that sample No. 6 showed the presence of colloidal material which failed to settle out after standing a period of eleven days. Clearness was not even obtained then after centrifugation at 2000 R. P. M. for a period of one hour.

It is noticed from Table IV that the radii of the particles of Clays Nos. 1 and 3 for the definite time intervals indicated are the same. This is due to the fact that the specific gravities of these two samples (Table II) are the same. The sedimentation curves for these two samples are different as seen in Figs. 2 and 4, due to the fact that there exists a difference in the per cent of the various sized particles in the two samples.

The data presented in this investigation are intended to apply to the specific clay samples studied and treated in the manner herein specified; however, the generalisations pointed out may be applied to any aqueous clay suspension.

THE ELECTROLYTIC PREPARATION OF THE ISOINDOLINES

BY E. W. COOK AND W. G. FRANCE

The isoindolines have usually been prepared by laborious methods^{1,2,3,4,5} which give rather poor yields.

The reduction of the phthalimide or the phthalimidine suggests itself as a likely possibility. However, attempts to carry out this reduction by the usual chemical methods have thus far been unsuccessful. Graebe⁶ using tin and hydrochloric acid was able to reduce the imide only to the imidine, the second carbonyl group being unattacked.

Hope and Lankshear⁷ in a preliminary report state that the preparation of isoindoline and methylisoindoline in high yields is possible by the electrolytic reduction of the corresponding phthalimidines, but nothing further has been published by them relating to this subject. Späth and Breusch⁸ describe the successful preparation of isoindoline by the electrolytic reduction of phthalimide.

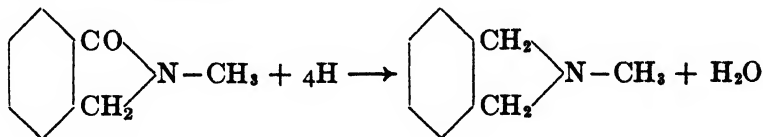
Sakurai⁹ prepared a hydroxy compound and phthalimidine from phthalimide in an alcoholic sulfuric acid solution at lead and copper cathodes, but not the further reduction product, the isoindoline.

The work of these investigators indicated the desirability of carrying on a further investigation of the electrolytic preparation of the isoindolines, and it was with this object in view that the present work was undertaken.

Experimental

PREPARATION OF METHYLISOINDOLINE

1. Reduction of Methylphthalimidine



The cathode materials used were mercury, lead, tin, and cadmium. A layer of freshly redistilled mercury of about 2 mm. thickness at the bottom of the vessel served as the mercury cathode. Connection was made with the

¹ Gabriel and Neumann: Ber. 26, 525 (1893).

² Gabriel and Pinkus: Ber., 26, 2210 (1893).

³ Scholtz: Ber., 31, 414, 627, 1154, 1700 (1898).

⁴ Frankel: Ber., 33, 2808 (1900).

⁵ Braun and Kohler: Ber., 51, 100 (1918).

⁶ Graebe: Ann., 247, 302 (1888).

⁷ Hope and Lankshear: Proc. Chem. Soc., 29, 224 (1913).

⁸ Späth and Breusch: Monatshefte, 50, 349 (1928).

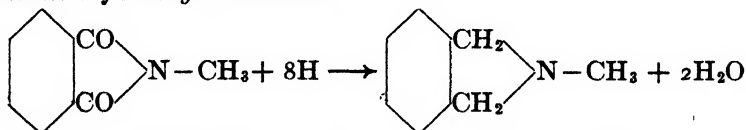
⁹ Sakurai: Bull. Chem. Soc. Japan, 5, 184 (1930).

mercury cathode by means of a stout platinum wire sealed into a piece of glass tubing which was also filled with mercury. The rest of the cathodes were sheets of the pure metal 4.5×5 cm. bent into a semi-circular shape of about 6 cm. diameter and 4.5 cm. height. The lead cathode was cut from commercial sheet lead and prepared according to the directions of Tafel.¹⁰ A platinum spiral anode was inclosed in a small porous clay cup and placed at the center of the semi-circular cathode. In the case of the mercury cathode the anode was placed about 2 cm. directly above the center of the mercury layer. For the catholyte 5 grams of methylphthalimidine was dissolved in a solution of 6 cc. of concentrated sulfuric acid in 102 cc. of water. During electrolysis the catholyte was vigorously stirred by means of an air driven stirrer. The anolyte contained 2 cc. of concentrated sulfuric acid in 20 cc. of water. The accompanying table indicates the other experimental conditions such as temperature and duration of electrolysis, as they were varied in the different experiments.

At the end of the electrolysis the catholyte was made alkaline with caustic soda and steam distilled until no more oily drops came over or until about 100 cc. of the distillate had been collected. A crystalline hydrate of methylisoindoline separated out in the distillate. This was filtered off and carefully dried in a desiccator. The hydrate melted at $45-45.5^\circ$ which agrees well with the value $45-46^\circ$ given by Braun.¹¹ The hydrate was readily dehydrated in a vacuum desiccator over sulfuric acid to give the free base which was a colorless oil having a strong basic odor. Upon standing in a closed vessel the base gradually assumed a darker color.

To further identify the compound the methiodide was prepared, which was identical with that prepared by Frankel¹² from isoindoline. The methiodide melted at $245-246^\circ$, turning to a dark color. This agrees with the value $244-245^\circ$, given by Frankel.

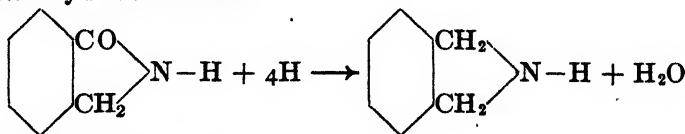
2. Reduction of Methyl Phthalimide



The procedure followed was similar to that for the imidine except that in this instance a suspension of the imide was used; the imide was quite insoluble, however, as the reduction progressed it gradually went into solution until at the end of about 7 ampere hours it had completely dissolved.

PREPARATION OF ISOINDOLINE

1. Reduction of Phthalimidine



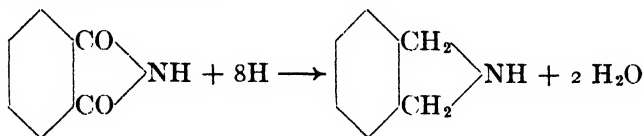
¹⁰ Tafel: Ber., **33**, 2215 (1900).

¹¹ Loc. cit.

¹² Loc. cit.

Not all of the 5 grams of the imidine used in the catholyte was dissolved and a small portion was left in suspension. This readily passed into solution early in the electrolysis. At the end of the electrolysis the catholyte was made strongly alkaline with solid sodium hydroxide and was steam distilled, the distillate being run into hydrochloric acid solution. Upon evaporation of the distillate the hydrogen chloride salt of isindoline remained. For identification the nitroso derivative was prepared which melted at $96.5\text{--}97.5^\circ$ as compared to the recorded¹³ value of $96\text{--}97^\circ$.

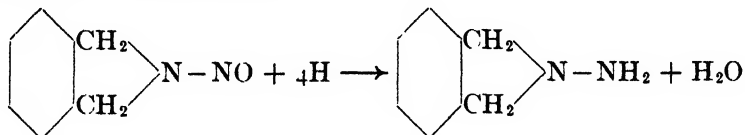
2. Reduction of Phthalimide



A suspension of 6 grams of phthalimide purified by sublimation was used in the catholyte. At the beginning of the electrolysis the catholyte was colored a greenish yellow, but at the completion was colorless.

PREPARATION OF N-AMIDOISOINDOLINE

Reduction of Nitrosoisindoline



About 5 grams of nitrosoisindoline recrystallized from dilute alcohol was used in the catholyte. After the electrolysis an ether extraction was made on the catholyte to remove any possible nitrosoisindoline that had escaped reduction. Then the catholyte was made strongly alkaline with solid sodium hydroxide and steam distilled into hydrochloric acid. This solution was evaporated almost to dryness when the hydrazine hydrochloride separated out. The hydrochloride was purified by recrystallizing from absolute alcohol. The yield of hydrazine was determined by oxidizing an aliquot portion of the catholyte with hot Fehling's solution and measuring the volume of nitrogen evolved. For identification the benzal hydrazone was prepared which gave a melting point of $127\text{--}129^\circ$ which agrees with that given by Frankel.¹⁴ With picric acid the hydrazine gives a picrate which melts at $96\text{--}98^\circ$.

Discussion of Results

It is remarkable that while no methylisindoline was obtained from methylphthalimidine at a tin cathode, a small yield was obtained from methylphthalimide. This is apparently analogous to the reduction of cam-

¹³ Gabriel and Neumann: Loc. cit.

¹⁴ Frankel: Ber., 33, 2812 (1900).

phoric-acid imide and camphidone reported by Tafel and Eckstein.¹⁵ They obtained the α and β camphidones and camphidine as reduction products of camphoric acid imide, but were unable to reduce camphidone itself to camphidine.

Tabulation of Results

Cathode	Time Hrs.	Temp.	Amp.	Volts	Current Density amp/dm²	Yield Efficiency	
						Material	Current
Reduction of Methylphthalimidine						%	%
Hg	6	11°	1	6	2.97	38.0	23.0
Pb	3	12°	3	5	4.66	57.1	23.1
Pb	5	46-49°	3	5.5	4.45	68.6	16.7
Sn	5.33	51°	3	5.2	4.45	100.0	100.0
Cd	5.33	53°	3	5	4.45	4.4	2.0
Reduction of Methylphthalimide							
Sn	10.67	49-51°	3	5.6	4.45	7.7	1.9
Hg	32.00	41°	1	5	2.97	31.1	7.8
Cd	10.67	46°	3	5.4	4.45	57.1	14.3
Pb	10.67	50°	3	5	4.45	57.7	14.4
Reduction of Phthalimidine							
Cd	5.33	49°	3	4.5-5	4.45	71.6	18.0
Pb	5.67	45°	3	5-6.5	4.45	64.3	15.3
Sn	8.67	52°	3	5.5	4.45	100.0	100.0
Reduction of Phthalimide							
Pb	10.67	50°	3	5.5-6	4.45	73.2	16.7
Reduction of N-nitrosoisindoline							
Pb	3.75	43°	3	5-5.2	4.45	72.0	21.1
Cd	3.75	44°	3	5-5.3	4.45	91.7	29.5

In accounting for their results they assume the camphidones to be extremely resistant towards further reduction and not to be intermediate products in the formation of camphidine. Furthermore they believe either that camphidine is formed only when both carbonyl groups of the acid imide are by accident simultaneously attacked by the reducing agent, or, that a carbinol-like intermediate product in which the second carbonyl group is electrolytically attackable, is already formed during the transformation of camphoric acid imide to camphidone.

The extension of this explanation to the analogous reductions of methylphthalimidine and methylphthalimide with tin cathodes leads one to conclude that no methylisindoline was obtained from methylphthalimidine for the following reasons:

¹⁵ Tafel and Eckstein: Ber., **34**, 3274 (1901).

- (1) Methylphthalimidine is incapable of undergoing further reduction;
- (2) In view of this great resistance to reducing action it is unlikely that the imidine would be an intermediate product in the electrolytic reduction of the imide to the isoindoline. This is given some support by the fact that no imidine was isolated when a reduction of the imide was carried out for the theoretical length of time;
- (3) Since the isoindoline is assumed to be formed only by the accidental simultaneous attack of two carbonyl groups by the reducing agent, it is obviously impossible for this to occur with the imidine which contains but one carbonyl group;
- (4) Likewise the possibility of the formation of a carbinol-like intermediate product is excluded since this also is assumed to be formed from the imide.

The successful reduction of methylphthalimide with tin cathodes would therefore be explained on the basis of either the accidental simultaneous attack of both of its carbonyl groups or the formation of a readily reducible carbinol-like intermediate product.

However plausible this explanation may be it loses most of its force when considered in the light of the results obtained with mercury, lead and cadmium cathodes. Thus for example, good yields of the corresponding isoindolines were obtained from methylphthalimidine at mercury and lead cathodes, and from phthalimidine at cadmium and lead cathodes. Evidently the imidines are not "resistant enough to further reduction" to avoid being reduced when mercury, lead and cadmium cathodes are substituted for tin.

Reference to the data for the reduction of methylphthalimide shows that the yields of isoindoline were from four to seven times greater when lead, cadmium or mercury cathodes were substituted for the tin cathode. Therefore, according to the suggested explanation of Tafel and Eckstein it would appear either, that the chances for the simultaneous attack of the two carbonyl groups of the imide are very much less at tin than at lead, cadmium or mercury cathodes, or that the hypothetical carbinol-like intermediate product is less readily formed at a tin cathode than at the lead, cadmium or mercury cathodes. Since direct experimental evidence is lacking in support of either possibility and especially in view of the fact that the imidines were reduced a more satisfactory explanation is needed.

In the absence of catalytic effects, a stronger reducing action is obtained at a cathode having a high hydrogen overvoltage than at one having a low hydrogen over-voltage. The order of decreasing hydrogen over-voltages in $\text{N.H}_2\text{SO}_4$ for the various cathodes used in this work is given by Caspari¹⁶ as mercury, lead, tin and cadmium. From this one would expect a weaker reducing action with tin than with lead or mercury cathodes. The differences in reducing energies as expressed by the hydrogen over-voltages of the metals, would reasonably account, on the one hand, for the failure to reduce the imidine and for the low yields obtained from the imide, when tin cathodes

¹⁶ Caspari: *Z. physik. Chem.*, **30**, 89 (1899).

were used; and on the other, for the successful reduction of the imidine and the higher yields from the imide when mercury, lead and cadmium cathodes were used. In the case of methylphthalimide the fact that the yields obtained at mercury having the highest over-voltage are lower than those obtained at cadmium having the lowest over-voltage may be the result of the catalytic activity of the metals.

Similar variations in results predicted on the basis of over-voltages have been frequently observed. Löb and Moore¹⁷ found that the reduction of nitrobenzene to aniline in a caustic soda solution proceeded better at a copper cathode than at metals of higher over-voltage.

Fichter and Stocker¹⁸ studying the reduction of phenol to cyclohexanol were able to effect the reduction at platinum and unable to at a lead cathode.

Bancroft and George¹⁹ have more recently investigated the electrolytic reduction of phenol and the catalytic hydrogenation of phenol vapor in the presence of platinum and nickel catalysts. They state: "The experiments of Fichter have been confirmed, that phenol is hydrogenated at a platinum cathode and practically not at all at a lead cathode, in spite of the high over-voltage of the latter. The effect of platinum in activating phenol is evidently more important than the reducing power of the hydrogen. . . . Platinum has a specific effect on the hydrogenation of phenol both when used as a cathode and as a catalyst."

In view of the influence of the over-voltage and catalytic activity of the metal cathodes in determining the course of a reaction, it seems that the results obtained in this work on the preparation of isoindolines can be more satisfactorily and reasonably accounted for on the basis of the hydrogen over-voltages and probable differences in the selective activation of the depolarizer by the various cathodes, than by the explanation offered by Tafel and Eckstein in connection with the reduction of camphoric acid imide.

If as suggested in the work of Bancroft and George²⁰ there is a probability that the oriented adsorption of the depolarizer is different at different metals, it is also probable that a relation may be found to exist between the lattice constants of the cathodes and the polar properties of the depolarizer. This point together with the factors such as, nature of surface, current density, duration of polarization, and previous treatment, which influence the over-voltage of the metals is being considered in connection with other electrolytic reductions now in progress in this laboratory.

Summary

1. Isoindolines have been prepared by the electrolytic reduction of methylphthalimidine, phthalimidine, methylphthalimide, and phthalimide.

¹⁷ Rideal and Taylor: "Catalysis in Theory and Practice," 2nd Ed., 428 (1926).

¹⁸ Fichter and Stocker: *Ber.*, **47**, 2015 (1914).

¹⁹ Bancroft and George: *Trans. Am. Electrochem. Soc.*, **57**, 399 (1930).

²⁰ *Loc. cit.*

2. N-amidoisoindoline has been prepared by the electrolytic reduction of N-nitrosoisoindoline.
3. Variations in the yields obtained with different electrodes have been attributed to the hydrogen over-voltages and probable differences in selective activation of the depolarizer by the metals.

The authors express their gratefulness to Dr. C. E. Boord of this Department for his continued interest and advice throughout the course of this investigation.

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THE ATOMIC MASS OF POTASSIUM

I. The End-point of The Potassium Chloride-Silver Titration*

BY CLYDE R. JOHNSON** AND GEORGE W. LOW, JR.

This article describes a method by which the potentiometer may be substituted for the nephelometer in finding the end-point of certain precise titrations. The method is a general one for a type of titration widely applicable in atomic mass measurements. The technique required is simple, yet it completely avoids "liquid junction" and "activity" difficulties which have hitherto offered an obstacle to the use of the potentiometer in analyzing the systems obtained in work of this nature. The use and scope of the new method may be inferred from the following record of potentiometric and nephelometric analyses of potassium nitrate-nitric acid solutions saturated with silver chloride. The liquids analyzed were similar in every respect to the solution in equilibrium with the precipitated silver chloride at the end-point of the potassium chloride-silver titration. The equilibrium point of this system at 0°C . is to be used as a reference end-point in a determination of the potassium chloride-silver ratio.

Experimental

The experiments consisted in analyzing the unknown saturated solutions for silver and chloride by comparison with standard solutions having almost the same composition. The standard and test systems were prepared from carefully purified reagents with all of the necessary precautions¹ to obtain solutions containing equivalent amounts of silver and chloride.

Typical Analytical Systems. Each of the two test systems was 0.600 molar in potassium nitrate, 0.308 molar in nitric acid, and contained 13.5 grams of fine-grained silver chloride. Before making up the systems, silver chloride No. 1 was allowed to stand in contact with dilute nitric acid containing a small amount of silver nitrate; silver chloride No. 2 in contact with dilute nitric acid containing a small amount of potassium chloride. These solutions were later washed out with portions of the nitric acid-potassium nitrate mixture.

The supernatant liquids of the typical analytical systems were brought to equilibrium at 0°C . and analyzed for silver and chloride. While still in contact with the respective precipitates, they were next titrated away from the end-point in opposite directions by known additions of silver nitrate and potassium chloride, and again analyzed.

Standard Solutions. Each standard solution was also 0.600 molar in potassium nitrate, and 0.308 molar in nitric acid, but contained chloride and silver equivalent to 0.600 milligrams of silver per liter. Suitable correction was

* Contribution from the Frick Chemical Laboratory, Princeton University.

** National Research Fellow in Chemistry.

¹ J. Phys. Chem., 36, 1942 (1932).

made for the nitrate and potassium added to the standards with the silver and chloride. For the sake of uniformity standard solutions of the same composition were used in all of the nephelometric and potentiometric analyses. It was recognized that this procedure would decrease to some extent the accuracy of the nephelometric analyses of the solutions not at the end-point.

The Analyses. The 4-liter glass-stoppered Pyrex bottles containing the test systems were packed in ice during the entire experiment, and a calibrated thermometer immersed in the solutions invariably registered 0.2°C . The

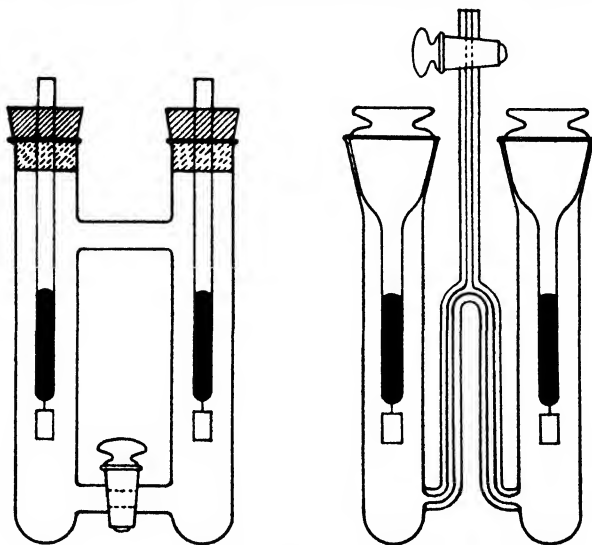


FIG. 1
Cells for E.M.F. Measurements

bottles were shaken once or twice only after the removal of test portions, otherwise twice each day.

For each set of six analyses an 80 to 100 milliliter portion of the cold supernatant liquid was withdrawn and filtered through a sintered glass mat. Two 20.00 ml. samples were analyzed nephelometrically for silver and chloride by the standard solution method.¹ Two 10 ml. samples from the same portion were analyzed potentiometrically for silver and chloride with the two cells:

Ag/Analytical Solution/Standard Solution/Ag

Ag/AgCl/Analytical Solution/Standard Solution/AgCl/Ag.

Two forms of cell suitable for the analyses are shown in Fig. 1. An essential feature of the design is that it permits one to join the solutions just before the E. M. F. measurements are made. The silver and silver chloride electrodes were prepared in the manner described by MacInnes and Parker,² with the modifications suggested by Carmody.³ However, the customary washing of the silver chloride electrodes with pure water was carefully avoided. For the measurements made at 0°C . the electrodes were placed in the cell only

¹ J. Phys. Chem., **35**, 830 (1931); **36**, 1942 (1932).

² MacInnes and Parker: J. Am. Chem. Soc., **37**, 1445 (1915).

³ Carmody: J. Am. Chem. Soc., **51**, 2901 (1929).

after it had been packed in ice for some time. In general, the electrodes were stored and rinsed in solutions of the composition in which they were to be used, and long exposure to the air was avoided.

A uniform procedure was adopted for the analyses. Each pair of electrodes was placed in a portion of the standard solution and short-circuited overnight. Following an initial E. M. F. measurement with the electrodes in the same solution, the electrodes were rinsed and allowed to stand in solutions of the composition in which they were to be used. The electrodes were then placed in position in the cell, and the analytical E. M. F. measurements were made, first at 0°C. and then at 25°C. Immediately following these observations, the contents of the cell were mixed and a final set of readings was made.

Each silver and each chloride analysis consisted of four E. M. F. readings taken over a period of thirty minutes after the cell had reached temperature equilibrium. Measurements made with Leeds and Northrup Type K and Students' potentiometers were equally satisfactory. The standard unsaturated Weston cell was compared with the laboratory standards. All of the work was done in the light of Series OA Wratten Safelights.

Discussion of Results

The initial E. M. F. readings were never greater than 0.15 millivolt and usually very much less. The final E. M. F. readings were generally about 0.2 or 0.3 millivolts. Silver analysis No. 2, System No. 2, in which the final value was 2.5 millivolts, was the only marked exception to this rule. Even in this case no correction was applied on the basis of the initial and final readings. However, there is every indication that it would be possible to make significant corrections of this nature which would improve the accuracy of the potentiometric analyses.

The results of the analyses are summarized in the following table. For the purpose of comparison, the chloride and silver concentrations in Table I are both expressed as milligrams of silver per liter. That is, the chloride concentrations have been multiplied by the factor Ag/Cl. The "silver added" in the third column gives the total silver which had been added to the system as silver nitrate, or "subtracted" as potassium chloride, at the time the analysis was made. The corresponding additions of these materials were both made on the 22d day of cooling.

The analytical E. M. F. readings were remarkably constant and reproducible. The four observations made over a period of thirty minutes rarely covered a range of more than 0.1 or 0.2 millivolts. Each value given in the appropriate section of the table is based on the average of four such readings, and is calculated from the expression: $\log C = E/0.0001984T + 0.778 - 1$. When the silver or chloride concentration, C , is expressed in milligrams per liter, as silver, E is in volts, and T is the absolute temperature. In either cell the electrode in the test solution containing excess chloride was negative, and the electrode in the test solution with excess silver was positive.

The limitations of the above expression in interpreting the E. M. F. data are recognized. The eight final chloride analyses made at 25°C. show the tendency of the silver chloride electrodes to dissolve and saturate the solutions

TABLE I
 Summary of Analyses

No.	Time cooled Days	Silver added Mg/Liter:	Nephelometric Analyses		Potentiometric Analyses:			
					At 0°C.		At 25°C.	
			Chloride	Silver	Chloride	Silver	Chloride	Silver
1	16	none	0.64	0.63	0.62	0.62	0.61	0.63
	21	none	0.61	0.61	0.62	0.64	0.61	0.66
	22	none	0.63	0.62	0.62	0.61	0.61	0.59
2	18	none	0.63	0.64	0.60	0.60	0.61	0.62
	20	none	0.59	0.63	0.61	0.67	0.60	0.65
	21	none	0.62	0.62	0.63	0.62	0.61	0.63
1	26	+0.300	0.54	1.02	0.49	0.78	(0.56)	0.77
	28	+0.300	0.55	1.01	0.51	0.79	(0.58)	0.71
	29	+0.300	0.52	0.84	0.49	0.75	(0.56)	0.64
	34	+0.300	0.55	1.02	0.49	0.77	(0.56)	0.77
2	25	-0.300	0.92	0.62	0.79	0.50	(0.66)	0.51
	28	-0.300	0.94	0.57	0.77	0.49	(0.67)	0.49
	29	-0.300	0.72	0.48	0.77	0.49	(0.65)	0.47
	33	-0.300	0.80	0.49	0.78	0.49	(0.65)	0.50

in the cell. It appears that this source of error does not appreciably affect the potentiometric analyses made at 0°C. Evidence for this belief may be found in the agreement of the first six nephelometric and potentiometric chloride analyses, and also in the symmetry of the sixteen values obtained by the potentiometric analysis, at 0°C., of the solutions containing excess silver and chloride. The fact that the potentiometric chloride analyses apparently give correct values at either 0°C. or 25°C., when both the standard and test solution contain equivalent amounts of silver and chloride, may mean only that the solution of the electrodes is accompanied by no electrical effect in this unique case. Nevertheless, the observations made by the method described in this article may be used in an actual titration as evidence that the end-point has been reached. Any possibility of serious error due to the solubility of silver electrodes in the 0.3 molar nitric acid is ruled out by the agreement of the first six sets of nephelometric and potentiometric silver analyses.

Equal-opalescence "analyses" made by the method of Richards and Willard,¹ incidental to the first six sets of analyses given in the table, yielded ratios from 1.35 to 1.65, all indicating that the solutions contained excess chloride. It seems that the method leads to a pseudo-end-point in the case of the potassium chloride-silver titration. Investigators who have attempted to determine the potassium chloride-silver ratio have generally used either the above equal-opalescence method or the still more unsatisfactory procedure of Richards and Wells.² This observation may have some bearing on the fact that authorities have been unable to agree consistently upon an accurate value for the atomic mass of potassium. Thus, in summarizing the results of the various determinations of the potassium chloride-silver ratio made over the

¹ Richards and Willard: *J. Am. Chem. Soc.*, **32**, 32 (1910).

² Richards and Wells: *J. Am. Chem. Soc.*, **27**, 459 (1905).

past quarter of a century by the classical Harvard methods, Baxter¹ concludes that "the atomic weight of potassium seems to be in some doubt."

It may be inferred from the data given in the above table that the standard solution method of analysis permits the excess or deficiency of silver in the analytical solutions to be determined to about 0.02 milligram for every ten grams of silver used, in the case of the potassium chloride-silver titration. The potentiometer may be substituted for the nephelometer in the analyses without loss of accuracy. That is, in so far as the determination of the end-point limits the experimental accuracy, it is possible to obtain analyses correct to one part in 500,000 by the use of the nephelometric or potentiometric procedures outlined in this report.

The present experiments give incidental information which is of interest in connection with the problem of making a precise adjustment to the end-point. The limitation placed on the accuracy of the eight final pairs of nephelometric analyses has been mentioned. In spite of this limitation, it seems very likely that the irregularities in the results of these analyses are in part due to the presence of colloidal silver chloride in the test systems. The additions of silver nitrate and potassium chloride must have resulted in the formation of small amounts of colloidal silver chloride under conditions in which it would be quite stable. The behavior of the colloidal material in the respective systems, on this interpretation of the analytical results, is in accord with Lottermoser's conclusion² that the positive silver chloride sol is more stable than the negative sol. On the other hand, it is of interest to note that the potentiometric silver analyses, at 25°C., of the same *unsaturated* solutions used in the nephelometric analyses, show no evidence of the presence of silver having its source in any such colloidal material. The potentiometric analyses at 0°C. would not be expected to reveal the presence of a colloid. Whatever interpretation is placed on the data, it is evidently advisable to minimize the removals of test portions in the titration. It is also sound practice actually to adjust the analytical solutions to the correct end-point, where the coagulation of the colloidal material is comparatively rapid. Conclusive evidence that the correct end-point has been reached may be obtained in any case by comparing the results of the nephelometric or potentiometric analyses with the predetermined solubility of the precipitated compound.

The problem of adsorption by the precipitated silver chloride has deliberately been avoided in the present work, as it is one of sufficient importance and difficulty to warrant separate treatment. While the analyses may seem to show that no measurable adsorption of silver nitrate or potassium chloride occurs, they are not necessarily conclusive, because of the preliminary treatment of the silver chloride samples. The analytical method used in these experiments would be very suitable for the study of adsorption effects by the examination of successive washings from the precipitated material, in an actual titration.

The authors take this occasion to express their thanks to Prof. N. H. Furman for his interest and co-operation in this work.

Princeton, New Jersey.

¹ Baxter: J. Am. Chem. Soc., 50, 617 (1928).

² Lottermoser: Alexander's "Colloid Chemistry," I, 673 (1926).

CHEMICAL ACTION IN THE GLOW DISCHARGE. X

The Decomposition of Nitrous Oxide

BY P. D. KUECK AND A. KEITH BREWER¹

The formulation of the principle underlying the electrochemistry of gases as presented in the previous articles of this series, has been confined almost entirely to the study of reactions involving synthesis. It becomes of interest, therefore, to see if the mechanism developed from these experiments holds for pure decomposition reactions, i.e., does the usual electrochemical equivalence law hold for both types of reaction; is the dissociation initiated by positive ions; are some ions much more efficient as reaction centers than are others; is the M/N ratio expressed by small numbers.

The decomposition of nitrous oxide is particularly suited for this investigation not only because it has been the subject of extensive investigations, but because it offers few complications to the glow discharge technique which has been developed.

Apparatus and Method

In the previous experiments it was possible to remove the products of the reaction as fast as formed by surrounding the discharge with liquid air. In the present case these products could not be removed by this means; it was necessary, therefore, to design a discharge tube which permitted a rapid diffusion of the gases so that the composition of the gas throughout the system would be comparatively uniform.

The tube used in determining the rate of decomposition is shown in Fig. 1A. The cathode was an aluminum disc one inch in diameter completely covered except on the face with a tightly fitting glass case to confine the discharge to the front surface. The anode was an aluminum rod one-quarter inch in diameter and enclosed in a glass case except at the end. The electrode separation was two millimeters; this eliminated the positive column and anode glow.

The nitrous oxide used in these experiments was obtained from the Ohio Chemical Co., and contained negligible impurities. The other gases were purified in the manner described in the previous article of this series.

The method of procedure for each series of runs was to fill the reaction system to a definite pressure, the partial pressure of nitrous oxide being varied from 100% to 10%. The progress of the reaction was determined by measuring the pressure change at fixed intervals of time, the discharge current being kept constant.

¹ Fertilizer and Fixed Nitrogen Investigations Department of Agriculture, Washington, D. C.

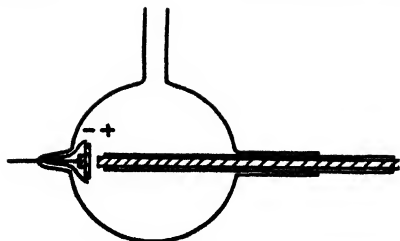


FIG. 1 A

Discharge tube for measuring the rate of decomposition.

The apparatus used to determine the concentration of the reaction products is shown in Fig. 1B. The discharge took place between the aluminum rods placed in an ignited soapstone housing in such a manner that the discharge was confined to a small pencil of glow through which the gas rapidly passed.

The condensable gases from the discharge were frozen out in a spiral immersed in liquid air; i.e., the undecomposed N_2O , the N_2O_3 , and the N_2O_4 . All NO formed in the discharge was converted into NO_2 and N_2O_3 in passing through the condensing trap. The concentration of NO_2 was determined by the light adsorption method at $150^\circ C$. The N_2O_3 was measured by the increase in light absorption upon the addition of oxygen to the condensed gas mixture.

The non-condensable gases (N_2 and O_2) were collected in an auxiliary discharge tube of the usual design. The amount of each gas was determined by measuring the quantity of NO_2 that could be synthesized from the mixture using the technique previously described.¹

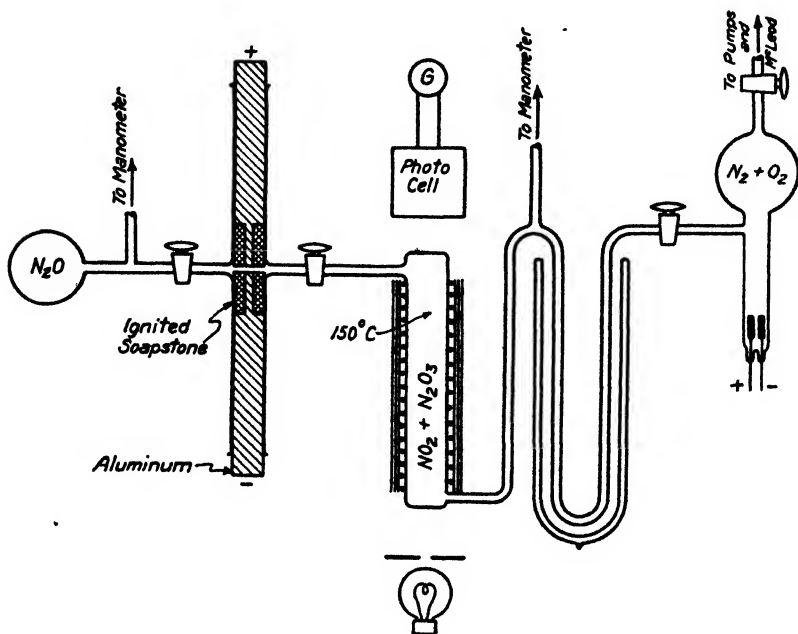


FIG. 1 B

Apparatus for measuring the relative concentrations of the immediate products of the decomposition.

¹ Westhaver and Brewer: *J. Phys. Chem.*, **34**, 554 (1930).

Results

The total pressure changes observed in each case showed the decomposition to go completely to the elements as a final product. The maximum rate of pressure change for each run appeared at the start of the run, the rate decreasing with time until no further change occurred at the pressure equilibrium to complete dissociation.

In experiments of this type there are several methods by which the rate of reaction can be determined. (1) The tangents to the pressure-time curves can be used as a measure of the rate; (2) the time for quarter or half decomposition can be used; (3) since the experimental results were such that a straight line was obtained when the log of the partial pressure of nitrous oxide was plotted against time, the rate can be derived directly from the slope of this line. The latter of the three methods was used, since it offered by far the greater accuracy.

The partial pressure of nitrous oxide at any instant was obtained as follows: The pressure in the system at time t is expressed by

$$P_T = p_{N_2} + p_{O_2} + p_{N_2O} = p_{N_2O} + 3/2(P_{O_2} - p_{N_2O}) \quad (1)$$

where P_T is the total pressure, P_{O_2} the initial pressure, and p refers to the partial pressures. From this

$$p_{N_2O} = 3P_{O_2} - 2P_T \quad (2)$$

The rate of reaction can be computed from the log p_{N_2O} -time curves since the results show

$$\frac{d \log p_{N_2O}}{dt} = S \quad (3)$$

Since $d \log p_{N_2O} = d p_{N_2O}/p_{N_2O}$, this expression becomes

$$\frac{d p_{N_2O}}{dt} = p_{N_2O} S \quad (4)$$

where $(p_{N_2O}S)$ is the rate. p_{N_2O} refers to the initial pressure in determining the initial rate for various pressures of pure nitrous oxide. Under these conditions the rate is constant, and S , therefore, is inversely proportional to p . The absence of any dependence of the rate on the initial pressure is due to the fact that the cathode fall of potential is constant over the pressure range investigated, hence the rate of positive ion formation is independent of the pressure over this range.

Factors influencing Decomposition. The initial rate of decomposition of nitrous oxide for various discharge currents is shown in Fig. 2. These measurements were made with an initial pressure of 5 mm. It will be seen that the rate of reaction is proportional to the current passing through the discharge.

The effect of the initial pressure on the rate is shown in Fig. 3. It will be observed that within the limits of experimental error the rate is independent of the pressure over a wide range.

The effect of nitrogen on the rate of decomposition is shown in Fig. 4. The current was maintained at 10 m.a., and the total initial pressure was 5 mm. in each instance. The rates observed for the various gas mixtures fell on a straight line showing the rate of dissociation to be proportional to the partial pressure of nitrous oxide.

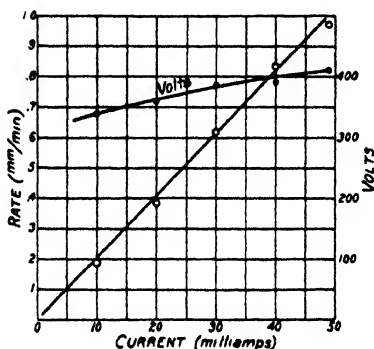


FIG. 2

The effect of the discharge current on the rate of decomposition.

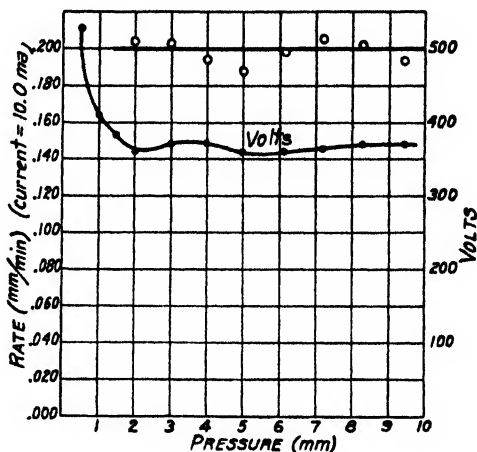


FIG. 3

The effect of pressure on the initial rate of decomposition.

The results obtained with added oxygen are very similar to those given for nitrogen, as can be seen in Fig. 5. It will be noted that the slopes of the two curves are identical, the principal difference being that both the voltage and rate curves for oxygen dropped slightly when the tube was "run in" with oxygen. It is interesting to note that an almost zero rate was observed

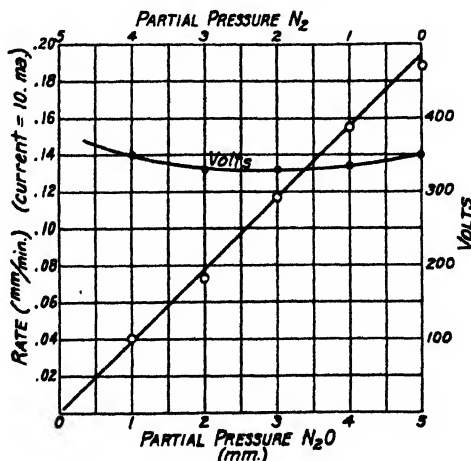


FIG. 4

The effect of nitrogen on the initial rate of decomposition.

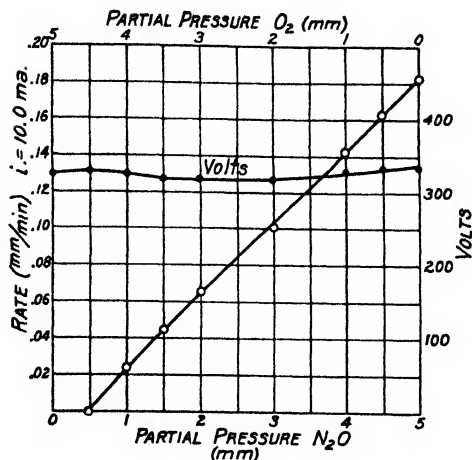


FIG. 5

The effect of oxygen on the initial rate of decomposition.

for a mixture composed of ten per cent nitrous oxide and ninety per cent oxygen. This is the only instance where no pressure change could be observed when nitrous oxide was present in the discharge.

The effect of argon on the rate of dissociation is shown in Fig. 6. The results differ from those obtained in nitrogen and oxygen in that argon materially lowers the cathode fall of potential and also that the decrease in rate due to the added argon is slightly more than a proportionality.

The results obtained in helium are illustrated in Fig. 7. It will be observed that the retarding action of helium is materially less than that given by a direct proportionality.

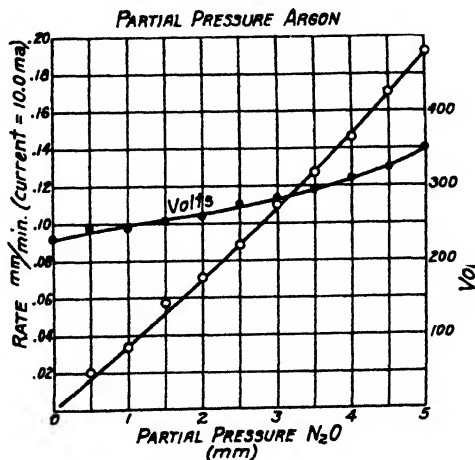
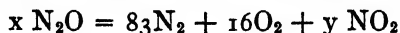


FIG. 6

The effect of argon on the initial rate of decomposition.

The Products of Decomposition. An analysis of the decomposition products showed them to be present in the same ratio irrespective of the current in the discharge, or of the pressure in so far as it could be varied. No attempt was made to determine the amount of nitrous oxide undecomposed. The results showed practically all the nitric oxide formed was oxidized to nitrogen dioxide in passing through the cooled trap; the amount of nitrogen trioxide formed was small. The final reaction was computed from the equation



where 83 and 16 represent the relative amounts of nitrogen and oxygen col-

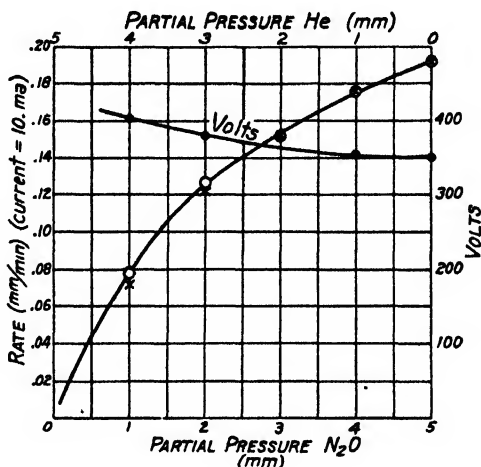


FIG. 7

The effect of helium on the initial rate of decomposition.
o = observed; x = computed

lected in the auxiliary discharge tube. A solution of this equation gives $x = 100$, and $y = 34$. The ratio of nitrogen to nitrogen dioxide is therefore 83 to 34 or 2.44 to 1.

Discussion of Results

The results which have just been presented on the dissociation of nitrous oxide in the glow discharge are in general agreement with those given previously for synthetic reactions as far as the electrochemistry of the discharge is concerned. Apparently the only differences observed in any of the reactions studied are in the M/N ratios, in the minimum number of collisions that an ion must make with neutral molecules for reaction to go to completion, and in the relative ability of various foreign ions to incite chemical action.

The data given in Figs. 2 and 3 show that the initial rate of dissociation is independent of the initial pressure between wide limits and is proportional to the current. Thus the rate may be expressed by the same electrochemical equivalence law given for synthetic reactions, i.e., $dP/dt = \alpha I$. It follows from this that the chemical activity results from primary processes occurring

in the discharge, the reaction being initiated by active states formed by direct electron impact; the interaction of excited states and the reactivity of states resulting from secondary processes are not appreciable. The simplest interpretation of these results is that used in the previous reaction studied, namely, that the reactivity takes place about the positive ions formed directly by the electrons ejected from the cathode.

A simple picture of the mechanism of formation of positive ions by electrons emitted from the cathode has been presented in the preceding article of this series.¹ In brief it was shown that the electrons leaving the cathode are accelerated by the cathode fall of potential through the Crookes dark space; this space is practically one ionization mean free path in length. The energy required is then expended by the electrons in the negative glow. Measurements of the rate of decay of reactivity in the negative glow show for mixtures of nitrogen and oxygen that the average path over which an electron is capable of inciting reactivity is 2.5 ionization mean free paths. The number of ions formed per electron of current is obtained directly from this value.

The relative ability of various ions to decompose nitrous oxide may be estimated from the results obtained in the presence of added gases. Thus Figs. 4 and 5 show the initial rate of decomposition in the presence of nitrogen and oxygen to be proportional to the partial pressure of nitrous oxide. It is not surprising, therefore, that the observed dissociation starting with pure nitrous oxide showed the rate at any time t to be proportional to the partial pressure of the gas remaining undissociated.

In a gas mixture containing nitrous oxide, nitrogen and oxygen, the ions are distributed among the three gases in proportion to their relative partial pressure times their efficiencies of ionization. The efficiency of ionization is defined as the average total number of positive ions formed per electron per cm. path at 1 mm. pressure and 0°C.² Unfortunately no accurate values are available for the probability of ionization in nitrous oxide; it is known, however, to be similar to that of nitrogen and oxygen. The observed fact that the initial rate of dissociation of nitrous oxide was always proportional to its partial pressure in mixtures containing various amounts of nitrogen and oxygen indicates that the ionization is distributed among the gases in proportion to their relative concentrations and also that the reaction is initiated primarily by N_2O^+ ions, the N_2^+ and O_2^+ ions being apparently ineffective.

These results may be expressed by the equation

$$\frac{dp_{N_2O}}{dt} = K \frac{\theta_{N_2O} p_{N_2O}}{\theta_{N_2O} p_{N_2O} + \theta_{N_2} p_{N_2} + \theta_{O_2} p_{O_2}} \quad (6)$$

in which θ is the efficiency of ionization and p is the partial pressure. The right hand term, therefore, gives the ratio of N_2O^+ ions to the total number of ions formed. Since θ is approximately the same for all three gases the rate of reaction is proportional to the rate of formation of N_2O^+ ions.

¹ Brewer and Kueck: *J. Phys. Chem.*, **36**, 2133 (1932).

² Compton and Van Voorhis: *Phys. Rev.*, **27**, 724 (1926).

Attention should be called to the difference between this expression and equation (5) for the rate of reaction for various initial pressures of pure nitrous oxide. S in the former expression is inversely proportional to p but K in the present instance is independent of P . Thus, since the total number of ions formed is independent of the pressure, the reaction becomes one of an apparent zero order, when only the initial rate for various total pressures is considered. On the other hand, the fact that the rate is proportional to p_{N_2O} for every separate run shows that the course of each individual reaction follows a first order expression, this is due to the fact that the reactivity is initiated primarily by N_2O^+ ions.

The results for argon differ from those of nitrogen and oxygen only in that the rate is just slightly less than proportional to p_{N_2O} . This decrease in rate is doubtless due to the lowering of the cathode fall of potential in the presence of argon. The value of θ_A is so close to that of θ_{N_2} for electrons of energy above 50 volts that its effect is negligible.

Helium differs from the other gases tried since the rate of dissociation is greater than that to be expected from the partial pressure of nitrous oxide. The ionization efficiency of an electron in helium, however, is materially lower than in the other gases discussed. Assuming the ionization efficiency to differ by a factor of two and one-half, as is the case for nitrogen and helium, the rate of decomposition as computed from the rate of production of N_2O^+ ions alone is given by the points marked x in Fig. 7. The increase in voltage due to the presence of helium is not considered in these calculations; this correction would tend to raise the computed values slightly where P_{N_2O} is small. The agreement between the observed and computed points is such that the conclusion can again be drawn that the rate of decomposition is determined by the rate of production of N_2O^+ ions, the He^+ ions being ineffective.

The Mechanism of Decomposition

It is evident from the result just presented that the rate of reaction is determined by the rate of formation of N_2O^+ ions, and that foreign ions and the secondary processes existing in the discharge have no apparent influence on the reactivity. Any speculation involving the mechanism of reaction around N_2O^+ ions necessitates a knowledge of the ratio of molecules decomposing to the number of ions formed, $M_{N_2O}/N_{N_2O^+}$.

In the preceding article of this series two separate methods were described for computing the rate of positive ion formation in the negative glow. The number of positive ions formed under conditions similar to the present ranged from 3.4 to 3.7 per electron of current. The positive ion current is negligible above 1 mm. pressure so may be neglected in the calculations. In the synthesis of nitrogen dioxide described in the previous paper reasons were presented for believing that the positive ions striking the cathode did not contribute to the reactivity. These factors, however, are not effective for decomposition reactions so no correction for the loss of ions need be made.

The number of molecules of nitrous oxide decomposed per electron is 14.5. Hence the ratio of molecules reacting to ions becomes $M/N = 14.5/3.7 = 3.92$, or 4.0 within the limit of experimental error.

The M/N values obtained from α rays¹ range from 1.74 to 4. Lind suggests the theoretical ratio of 2 for clusters neutralized by electrons and 4 for clusters neutralized by negative ions. The latter concept, however, can not be applied to the glow discharge since the rate of negative ion formation is too slow in comparison with the time necessary for a positive ion to reach the walls. Loeb² gives 6.1×10^5 collisions between an electron and nitrous oxide molecules as the number necessary for attachment.

The mechanism of reaction around the N_2O^+ ions, therefore, must be either through a cluster of the form $(4N_2O)$, or one involving steps or limited chains. The evidence is insufficient for a determination of the final mechanism, but the fact that the M/N ratio is independent of the initial pressure favors the straight cluster concept in preference to most types of secondary processes. Further, it is difficult to devise a chain mechanism not involving nitrogen in the form of atoms, excited molecules, or ions. If any of these contributed to the reaction chains, the rate, as shown by Fig. 4, would not be inversely proportional to the amount of nitrogen present.

Again, the mechanism postulated by Gedye³ in which it is suggested that decomposition is occasioned by excited oxygen cannot be correct in the present case, since the reaction is definitely retarded below that given by a proportionality to p_{N_2O} for high oxygen concentrations. Gedye, also, is forced to assume the thermal dissociation of two nitrous oxide molecules by collision with the activated products of reaction of each ion in order to account for an $M/N = 4$ ratio. The fact that the rate is independent of the total pressure as well as proportional to p_{N_2O} in the presence of various foreign gases capable of absorbing energy makes the possibility of the existence of a thermal mechanism highly problematical.

It is possible for a cluster of the $(4N_2O)^+$ type to dissociate in several ways, and hence it is not surprising that the various investigators using different methods of dissociation have observed considerable differences in the relative concentrations of the reaction products. Wourtsel⁴ expressed the primary reaction as $4N_2O = 3N_2 + 2NO_2$ for α ray decomposition. Joshi⁵ using the silent electric discharge suggests two modes of dissociation, the first and principal method being that given by Wourtsel and the second a straight decomposition expressed by the equation $2N_2O = 2N_2 + O_2$.

In the present experiment, where the reaction products were removed immediately from the sphere of reaction and where the pressure was much

¹ Lind: "Chem. Effect of α Particles."

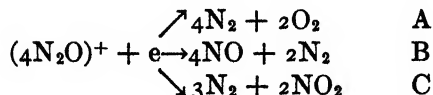
² Loeb: "Kinetic Theory of Gases."

³ G. B. Gedye: *J. Chem. Soc.*, 1931, 3016.

⁴ E. E. Wourtsel: *Le Radium*, 11, 289 (1919).

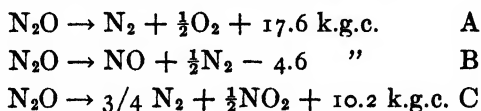
⁵ Joshi: *Trans. Faraday Soc.*, 25, 118 (1929).

lower than that used by Wourtsel and by Joshi, the reaction is expressed by the equation



in which the probability for A occurring as given by the concentration of the reaction products is approximately two times that for B, or one-half times that for C.

The energy changes involved may be an important factor in directing the mode of dissociation of the clusters, as well as in determining the M/N ratio. Reasonable values for the energy changes are



Unfortunately it cannot be told from the data whether the principal reaction is A and B, or A and C. It is true that no free NO was observed and that the N_2O_3 was never present in any appreciable amounts; however, there was always an excess of oxygen present and since the rate of oxidation of NO is high at liquid air temperatures the possibility of finding free NO or N_2O_3 is necessarily small. The fact that B is endothermic does not preclude its possibility since the N_2O^+ ions itself possesses some 320 k.g.c. of energy.

There is not sufficient evidence at present to permit the drawing of any definite conclusion regarding the dependence of the M/N ratio on the heat of reaction and on temperature. The limited data available, however, indicate a larger ratio for highly exothermal reactions. For instance, the oxidation of hydrogen and methane show twice the ion efficiency found in the case of the synthesis of nitrogen dioxide and ammonia. The intermediate value found in the present case is, therefore, in line with what might be expected from the heat of dissociation.

In discussing the decomposition of the $(4\text{N}_2\text{O})^+$ clusters nothing has been said concerning whether the neutralization occurs at the walls or in the gas phase. In discharge tubes of the type illustrated at the right in Fig. 1B it has been shown by direct experiment that the molecules synthesized reach the walls carrying a positive charge;¹ gas phase neutralization is negligible in the negative glow. A discharge tube of the type shown in Fig. 1A however, permits a greater opportunity for gas phase neutralization of the ions. Even here, however, the chance for this type of neutralization to occur is small except in the case of excess oxygen, where the concentration of O_2^- ions becomes appreciable. It will be observed in Fig. 5 that the rate is negligible in mixtures of 90% oxygen and 10% nitrous oxide, and also that the rate curve bends downward with an increasing partial pressure of oxygen. These lowered yields⁷ evidently result directly from the presence of gas phase

¹ Brewer and Kueck: J. Phys. Chem., 35, 1281 (1931).

neutralization wherein the M/N ratio is smaller than that observed for wall neutralization. This change in ratio occasioned by the mode of neutralization may account for the fact that the values given for α rays vary from 1.7 to 4.0, depending on the conditions of the experiment.

Summary

The rate of decomposition of nitrous oxide in the glow discharge is independent of the initial gas pressure and is proportional to the current. It may be expressed, therefore, by the general equation for the electrochemistry of gases, namely $dP/dt = \alpha I$. These results are interpreted to indicate that the reactivity is initiated by positive ions formed in the discharge.

The effect of added nitrogen, oxygen, argon, and helium on the rate of reaction was always such that the proportionality between the observed rate and the rate in pure nitrous oxide was equal to the relative concentration of N_2O^+ ions formed in the mixture and in the pure gas. Thus the reaction appears to be initiated by N_2O^+ ions, and to be little affected by N_2^+ , O_2^+ , A^+ , or He^+ ions.

The ratio of $M_{N_2O}/N_{N_2O} = 4$ was obtained, the error involved in the calculation appears relatively small.

An analysis of the initial decomposition products showed that the cluster decomposes in part directly into N_2 and O_2 and in part either into NO_2 and N_2 or into NO and N_2 , the data not being sufficient to decide between the two processes.

I. MOLECULAR WEIGHT IN DIFFERENT STATES OF AGGREGATION

BY G. ANTONOFF

I. INTRODUCTION.

The notion of molecular weight has been established as a result of work with gaseous matter, and owing to the Avogadro hypothesis it has become possible to express the same in definite units. Thus, when the matter is in a gaseous state, there is a rational method permitting to determine experimentally the molecular weight of a substance.

But as soon as the matter is presented in another state than the gaseous, nothing definite is known about its molecular state, and the difficulty is in the want of methods for its determination. This problem, however, important it appears to be, is very little advanced yet, in spite of the fact that there is quite a lot spoken about it in the literature. The substances in the liquid state are believed to be, according to the prevailing view, either "normal," if their molecular weight is said to be the same as in the gaseous state, or "associated" when the molecular weight is supposed to be a certain multiple of that in a gaseous state.

These views, however, are based on a number of empirical rules, whose theoretical foundation is very poor. Besides, their agreement with facts is also highly illusory.

Under such circumstances, it is nowadays realised by some authors that one cannot continue like that, that accumulation of empirical rules does not lead us anywhere, and that some general principle is necessary, a principle analogous to that of the Avogadro hypothesis,¹ which would give a rational solution of the problem for other than the gaseous states.

The object of this work is to propose such a principle on a basis of an evidence, which appears to some people *too simple to be true*, as the immense amount of work previously done has created the belief of an extreme complexity of the problem; I therefore come across difficulty in convincing other people, especially as the results obtained are in contradiction with such theories as that of van der Waals, whose views are accepted by many people as a Gospel. And yet his theory, in spite of the enormous amount of facts accumulated has not given the solution of the problem of the molecular weight of liquids at all.

I treat the subject quite differently on the whole, but I accept together with van der Waals the existence of molecular forces, which account for the surface tension in matter of all states of aggregation. I arrive at quite different results.

¹ W. E. S. Turner: "Molecular Association," 4 (1915).

To follow the views expressed in the following pages, it is, therefore, necessary to place one-self in an entirely different point of view, and no compromise appears to be possible between the two.

However, I must add, that the views I was led to are by no means novel. They can be shown to have some features of the theory of De Heen, which was completely abandoned and superseded by that of van der Waals. The reason of it is chiefly due to the fact that at the time there was not enough experimental or other evidence to serve as a foundation to his theory. His theory may be called a chemical theory.

When I started this work, I had an entirely open mind and for quite a long time I worked without any theory of my own. On a basis of experimental evidence, I was led to such deductions, which enabled me to establish a general principle, which is incompatible with the van der Waals theory. At the same time, it unquestionably leads to a kind of a chemical theory, and permits making deductions which are in perfect agreement with the experimental evidence. Moreover, it gives an explanation for some important facts which remained unnoticed merely for the reason that the accepted theories did not allow any room for them.

On the other side, the empirical rules, such as the relation of Eötvös—Ramsay and the like show a very poor agreement with experimental evidence, so poor that it is necessary to shut one's eyes not to see that this relation is not a representation of a true law. It is often possible to force the experimental figures into an empirical formula, but the closer examination of errors will immediately disclose the falsehood of it.

On the contrary anybody who wishes to verify some of my results and repeat some of my calculations, will see at once that *they are strictly exact* and conform with the experimental data within the limits of experimental errors in the proper sense of this word.

I have been recently criticised on the ground that I am alone who has arrived at such results, as exposed in the following chapters.¹ To this I must add that apart from De Heen a number of present day authors arrived at similar views, such as Drucker,² Harver,³ Duclaux⁴ and some others. One can also add that the recent investigation by means of X-rays by Katz⁵ is also in favour of such views and is against the theory of van der Waals. According to Katz it gives "*une image de la structure des liquides bien différente de celle qui nous avait donné jadis M. van der Waals.*"

Thus, the novelty of my work lies not so much in the views I arrived at, as in the general principle which leads to them. Owing to it, in the subject which appeared hopelessly complicated, everything becomes extremely simple, and so far I have not come across a single case amongst the material I investigated, which would be in disagreement with my theory.

¹ G. G. and I. N. Longinescu: Soc. Roumaine des sciences, **33** (1931).

² Z. physik. Chem., **68**, 616 (1909).

³ J. Phys. Chem., **16**, 451 (1912); **17**, 386 (1913).

⁴ J. Phys., [6] **5**, 33 (1924); **8**, 336 (1927).

⁵ Réunion Internationale de Chim. Phys., Activation et structure des molécules, Paris, 408 (Oct. 1928).

This theory can be expounded in different ways, but for the time being I prefer to follow the different stages in the order which corresponds to the natural development of this theory. It originated in such a way that I began to work out a certain theory of surface tension with the view of explaining some experimental results of mine. This theory is on the whole conformable with the classical theories; in other words, I operate with the same notions, putting them in a somewhat different shape, and it will be reproduced in the following chapter, starting from the first principles. This theory, quite unexpectedly, has led me to the conclusions which resulted in the theory of states of aggregation, as exposed in the following chapters.

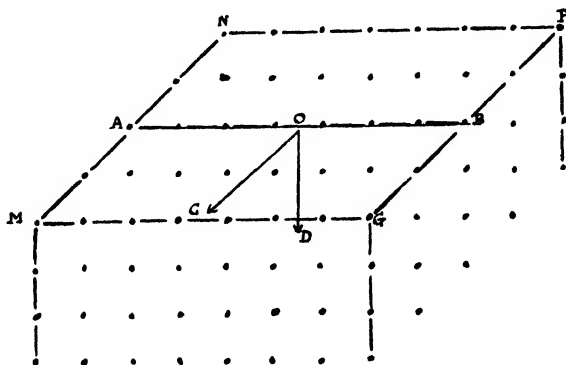


FIG. 1

II. SURFACE TENSION AND MOLECULAR STRUCTURE.

Imagine a crystal of rectangular form, which consists of molecules at an equal distance from one another. This is represented by dots in Fig. 1. I take a case of a non-polar substance where each dot represents a molecule, and not an ion, as in the case of sodium chloride, the case which was treated in detail by Max Born.¹ Each molecule is supposed to exercise a uniform field of force, no matter what is its nature, which may be different in various cases.²

This hypothesis is not the only one possible. But the result obtained remains substantially the same, and independent of the actual form of law of attraction. For this reason I limit this investigation to one form only.

Imagine a line AB in the surface, connecting one row of molecules. The adjacent rows of molecules will exercise a pull on the line AB. Consider at first only the forces acting in the surface MNPG tangentially to it. The effect of molecules situated on one side of the line AB, summed up together, is resulted in a force OC, which is generally called the surface tension.

It can be shown in a similar way that owing to the presence of molecules situated below the surface MNPG, there will be also a pull exercised on line AB in the direction perpendicular to OC and acting, inwards, represented in the drawing by the line OD. It will be of the same order of magnitude as OC

¹ Sitzungsber. preuss. Akad. Wiss., 48, 901 (1919).

² J. E. Lennard-Jones: Proc. Phys. Soc., 43, 461 (1931).

and will be somewhat bigger, as molecules on either side of the line AB will act jointly in this case. The field of force, according to the prevailing theories is of such nature that the force varies inversely as a high power of the distance. Consequently in the summing up of the forces due to individual molecules, the adjacent row of molecules will contribute the most important term in the sum. The total force acting on the whole surface MNPQ inwards will be obtained by summation of forces acting on all rows in the surface. *This inward force per unit area of the surface is generally called molecular, or normal pressure.*

It thus appears that if the number of molecules and their distance from one another is known, one can easily derive the normal pressure from the breaking stress of the crystal, and thereby also, calculate the surface tension.

However, in practice, it is not possible to proceed in this way, as one gets ridiculously low figures from the breaking experiments,¹ incompatible with other evidence. This is generally attributed to the fact that the crystal is never perfect and always has small invisible cracks, which diminish the resistance to traction to a considerable extent.

For these reasons, Born² in trying to estimate the surface tension of rock salt proceeded in an inverse way: he determined the compression of a crystal under external pressure. He has arrived at the conclusion that there exist also repulsive forces making themselves felt at compression, owing to which the substance resists to further compression.

I do not intend to use this method experimentally, and I therefore assume for the sake of argument that I am dealing with an ideal crystal. I denote by F a balance-force existing between two adjacent molecules at a distance d , where d is the intramolecular distance. This resultant force is equal to the difference between the attractive and repulsive forces and at a distance d it is positive, i.e. is an attraction.

If the distance between two adjacent molecules is d , in a length md there will be m molecules. Per unit length there will be $1/d$ molecules. Let the number of molecules per unit volume be n . Then, $1/d = n^{1/3}$.

The expression for surface tension can be found as follows.

Imagine two rows of molecules, as in Fig. 2.

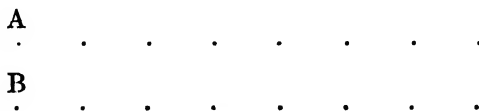


FIG. 2

Force between A and B = F

Between A and the adjacent row commencing with B, the force will be:

$$F + AF + BF + \dots = F(1 + A + B \dots), \text{ where}$$

A, B, etc. . . . are rapidly diminishing terms, if the force diminishes rapidly with the distance.

¹ Antonoff: Phil. Mag., **44**, 63 (1922); Z. physik. Chem., **102**, 388 (1922).

² Loc. cit.

The whole attraction of one row by the other will be then:

$$\begin{array}{l}
 F + AF + BF + CF + \dots \\
 F + 2 AF + BF + CF + \dots \\
 F + 2 AF + 2 BF + CF + \dots \\
 F + 2 AF + 2 BF + 2 CF + \dots \\
 \cdot \quad \cdot \quad \cdot \quad \cdot \\
 \cdot \quad \cdot \quad \cdot \quad \cdot \\
 \cdot \quad \cdot \quad \cdot \quad \cdot \\
 F + 2 AF + 2 BF + CF + \dots \\
 F + 2 AF + BF + CF + \dots \\
 F + AF + BF + CF + \dots
 \end{array}$$

The summation gives:

$$Fn^{1/3} + 2 A Fn^{1/3} - 2 AF + 2 BFn^{1/3} - 4 BF + 2 CFn^{1/3} - 6 CF + \dots$$

Only terms containing $n^{1/3}$ need be kept, n being of the order of 10^{21} , which gives:

$$Fn^{1/3}(1 + 2 A + 2 B + 2 C + \dots) = Fn^{1/3} K$$

This is the expression for attraction of two adjacent rows.

This is not yet the expression for surface tensions as on either side there are other rows of molecules which ought to be taken into consideration. Also the rows of molecules below the surface. All these summations will be of similar character and will ultimately lead to an expression of the same type, having the constant somewhat different from that in the expression just deduced. Thus, with sufficient accuracy one may assume that the surface tension (α) is equal to:

$$\alpha = K Fn^{1/3} \quad (1)$$

Thus, the surface tension appears to be a simple function of n — the number of molecules per unit volume, the quantity which is as important for the liquid and solid states, as the Avogadro constant for the gaseous state.

Now, proceeding in a similar way, one can also deduce the expression for the normal pressure.

Assuming that the field of force is uniform, it can be seen that the inward force on a row of molecules per unit length OD will be practically the same as the force acting in the surface tangentially to it, OC in Fig. 1, and will only have a slightly different constant. Its effect per unit area of the surface, as the normal pressure is generally expressed, will be then obtained by summation of forces due to all rows of molecules per unit area.

Thus, if we denote the normal pressure by P ,

$$P = K Fn^{1/3} \times n^{1/3},$$

where K is not the same as in expression (1), or

$$P = K Fn^{2/3} \quad (2)$$

From expressions (1) and (2) it follows:

$$P = K \alpha n^{1/3} \quad (3)$$

where K is not the same as before. This equation establishes the relation between the normal pressure and the surface tension for a crystal.

The same theory can be applied to the liquids with the difference that in this case, the above magnitudes will acquire *statistical values*.

Owing to kinetic effects there can be no question of any definite position of molecules at a determined distance. The conditions on the surface will be also complicated by the fact that the molecules with the speeds above the average will leave the liquid and spread in the surrounding space in form of a vapour. The formation of vapour is probably the reason why the normal pressure of liquid cannot be measured in a direct way as a breaking stress of a column of liquid. A slight presence of gases causes a formation of vapour, which disturbs the experiment. Thus, the normal pressure of a liquid cannot be measured in a direct way. But, the surface tension of a liquid can be deduced from the breaking stress of its film, which constitutes a beautiful method whereby it is measured in the form which follows directly from its definition.¹

Thus, the equations just deduced (1), (2) and (3) appear from the first sight to be of not much use, considering that the surface tension (α) alone can be measured experimentally.

Thus, although these formulae indicate a simple relation between the surface tension and n —the number of molecules per unit volume—we are not yet in position to determine the same. It was shown by myself in some other² publications, that the surface tension of a solid can be determined by measuring the field of force more or less directly. This method does not involve the quantity n , and the surface tension can be deduced without the knowledge of the same.

If one compares the value obtained by this method for rock salt, and that calculated by Born, under the assumption that it has the structure as indicated by the X-ray method, there appears to be a certain contradiction which is probably due to the fact that the molecular weight of the solid is not what it is assumed to be. Some experiments of W. H. Bragg seem to corroborate this view.³

It will be shown later on, that in special circumstances these equations can be solved all the same and thus important information can be derived as to the molecular weight of matter in different states of aggregation.

It will be seen that this can be attained by applying the above equations to systems consisting of different phases in equilibrium with one another. For purely methodical reasons, the easiest way of proceeding is to use systems capable of separating into two liquid layers. Their properties will be described in the following chapter and it will be indicated in what manner their properties can serve for the solution of the above problem.

¹ This is the justification of my method of procedure, as I am interested mainly in liquid systems. If I wanted to deal with solids, I would have to proceed in the same way as Born.

² Phil. Mag., 2, 1258 (1926); 3, 792 (1927).

³ Nature, 111, 428.

III. EQUILIBRIUM BETWEEN TWO LIQUID LAYERS.

The formation of two liquid layers takes place very much in the same manner as when a solid powder is suspended in a vehicle, i.e. in a liquid of some sort. The solid matter after having settled down will form a bottom layer, if it is specifically heavier than the liquid, or a top layer if it is lighter. But in both cases the particles of the solid are suspended in a vehicle.

Something similar takes place when the matter forming another layer is a liquid. Particles of it are distributed among the particles of the other, this latter liquid assuming the rôle of the vehicle, or a solvent as it should be called in a case of true solutions. This is illustrated in the adjoining drawing, representing schematically a vessel containing two liquid layers. The space

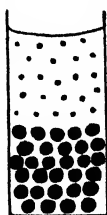


FIG. 3

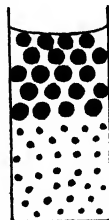


FIG. 4

left blank represents the vehicle. The particles of the liquid represented by big dots form a bottom layer in Fig. 3 and the top layer in Fig. 4. The small dots represent the particles of vapour.

The liquid thus suspended sends its vapour into the remaining part of the vehicle, as well as into the outside space. It is convenient for sake of argument to have the two layers enclosed into a ring-shaped vessel. Then both layers will have a free surface in contact with the vapour. This vapour must obviously be the same for both layers, otherwise there would be a perpetual distillation. Thus from consideration of equilibrium the both layers must have the same vapour pressure,

$$p_1 = p_2,$$

where p_1 is the vapour pressure of one layer and p_2 that of the other.

Both vapours must be obviously also of the same composition. This is known under the name of the law of Gibbs-Konovalov.

It should be pointed out that two liquid phase systems such as ether and water are generally spoken of as a solution of ether in water (lower layer) and a solution of water in ether (upper-layer). Investigation of properties of such systems shows that this is not the case at all. The only way to explain their properties is to assume the view as above, i.e., *that both layers are solutions in the same solvent*. In mixing two liquids with limited solubility, it is not possible to say which of them will play the rôle of a vehicle, or a solvent in the case of true solutions, by simply looking at them. This can be concluded by observing the freezing point curve of the system, Fig. 5. This curve is very typical for the systems forming two liquid layers. It indicates that both

liquid layers give off the same ice. It can be also seen that the curve always contains an eutectic point. The two concentrations A and B corresponding to two saturated solutions, constituting the upper and the lower layer, are situated on one side of the eutectic point. This, together with the fact that they separate the same ice, indicates that both layers are solutions in the same solvent.

If two solutions in the same solvent have the same freezing point, the same vapour pressure,¹ Fig. 6, they must contain the same number of molecules dissolved per unit volume, according to the elementary theory of solutions. The theory of solutions, however, is in most cases valid only for dilute

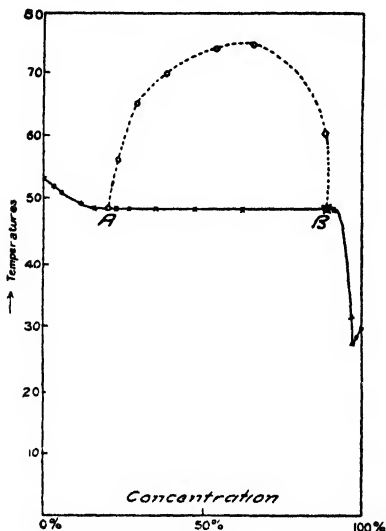


FIG. 5

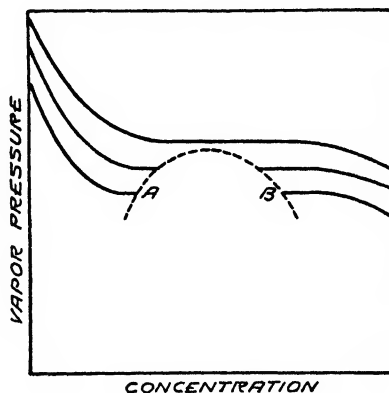


FIG. 6

solutions, although there are known cases when the ideal laws hold true also in concentrated solutions. The causes of these deviations not being exactly known, one must be careful in drawing conclusions. Although the elementary theory indicates that the two solutions contain an equal number of molecules, I do not want to accept it, unless this same can be corroborated by independent evidence. This can be derived from conditions of equilibrium expressed in terms of surface tension.

I found experimentally in 1907² that in a state of equilibrium, the following law can be found to be true:³

$$\alpha_{12} = \alpha_1 - \alpha_2, \quad (4)$$

where α_{12} is the interfacial tension, α_1 and α_2 the surface tensions of two satu-

¹ In Figs. 5 and 6 the dotted curve is the so-called solubility curve, within which the system consists of two layers. Outside it the system is homogeneous. Points A and B correspond to saturated solutions constituting the two superposed layers.

² Antonoff: J. Chim. phys., 5, 372 (1907).

³ It may be mentioned here that in the course of time, a number of authors tried to repeat my work, and some of them without success. This problem presents great difficulties experimentally. It is not always easy to choose an appropriate method. It is often very difficult to obtain and maintain equilibrium in the course of work. Besides that, some of them did not fully realise the meaning of equilibrium between two phases. As this matter is important, I treat it in a separate paper, *Kolloid-Z.*, 59, 7 (1932).

rated layers against their common vapour. I generally call it the "law of difference."

Now making use of the formulae (1) (2) and (3) of the foregoing chapter, one can deduce this law and demonstrate its theoretical significance.¹

One can take it for granted that when two liquid layers are in equilibrium, the relation

$$p_{12} = p_1 - p_2 \quad (5)$$

will hold true, where p_1 and p_2 are the normal pressures of the two liquid phases, and p_{12} is the resultant force. It was shown on p. 2410 that the relation between the normal pressure and the surface tension is of the form

$$p = K\alpha n^{1/3}, \quad (3)$$

where α is the surface tension and n is the number of molecules per unit volume, and K is a constant. On a basis of the equation (3), one can express (5) as follows:

$$\begin{aligned} P_1 &= K\alpha_1 n_1^{1/3}, \\ P_2 &= K\alpha_2 n_2^{1/3}, \\ P_{12} &= K\alpha_{12} n_{12}^{1/3}, \\ &\text{or} \end{aligned}$$

$$\alpha_{12} n_{12}^{1/3} = \alpha_1 n_1^{1/3} - \alpha_2 n_2^{1/3}$$

The expression becomes identical with

$$\alpha_{12} = \alpha_1 - \alpha_2, \quad (4)$$

assuming that the value of K^2 is the same in all cases, if

$$n_{12} = n_1 = n_2.$$

It may be pointed out that:

$$\alpha_{12} = \alpha_{21} \quad \text{i.e.}$$

one gets the same result if one measures α_1 against α_2 or inversely, α_2 against α_1 .

Consequently

$$n_{12} = n_{21}, \quad \text{i.e.}$$

on both sides of the surface of contact the molecular concentration is the same, and it is equal to that at the free surface of both layers. It is obvious that n_1 and n_2 comprise the number of particles of the solvent, which is obviously the same in both layers. This investigation shows that n molecules of one kind

¹ It should be mentioned that these equations were deduced for pure substances. Now we will deal with heterogeneous systems. I take it for granted that the magnitudes involved are a rectilinear function of molecular concentration. So that in the following investigation all K , α and P with indices and without will represent values obtained by the rule of mixtures. This assumption appears justified in cases where there is no chemical action between molecules, that is to say, when we have exact information as to the number of molecules in the system.

² One can see from the theory of surface tension as on p. 2410 that K depends on the distance between the particles. As we have to deal with equimolecular systems, K must be the same in the above cases, provided the molecules occupy the same volume in both layers, or else their volume is negligible compared with the intramolecular distance. I assume that this must be actually the case, as in all systems I investigated, I never came across cases where these phenomena might make themselves felt.

(1) and n molecules of another kind (2) are each distributed between m mols of solvent. Let γ be the surface tension of the solvent.

γ_1 be the surface tension of the system composed of mols (1)

γ_2 be the surface tension of the system composed of mols (2)

Then the surface tension of one solution α_1

$$\alpha_1 = \frac{\gamma m + \gamma_1 n}{m + n}.$$

The surface tension of the other solutions α_2

$$\alpha_2 = \frac{\gamma m + \gamma_2 n}{m + n}, \text{ and}$$

$$\alpha_1 - \alpha_2 = \frac{\gamma m}{m + n} - \frac{\gamma m}{m + n} + \frac{\gamma_1 n}{m + n} - \frac{\gamma_2 n}{m + n}.$$

Thus, the factor contributed by the solvent, being the same in both systems, disappears in the difference $\alpha_1 - \alpha_2$.

Let us assume now that the solvent vanishes from the system, everything else remaining the same, i.e., $m = 0$.

Then

$$\alpha_1 - \alpha_2 = \gamma_1 - \gamma_2.$$

The meaning of this speculation will be seen on p. 2419, whereby the rectilinear form of relationship appears quite justified.

The surface concentration according to existing theories, may sometimes differ from that at the interior of the solution.

Consider first the simplest case, when the concentration of the surface layer is the same as at the interior. In such case, the two liquid layers must be equimolecular, i.e. *they contain equal number of molecules per unit volume*, and this is the condition under which the law (4) of difference must necessarily be true.

If the surface concentration differs from that at the interior, the same must apparently be the case, for the following reason: we saw that both layers in equilibrium must have the same vapour pressure and the same composition of vapour. The change of molecular surface concentration therefore must be the same for both layers. And the two layers also in this case must be equimolecular.

Thus the conditions:

$$\begin{aligned} p_1 &= p_2 & \text{and} \\ \alpha_{12} &= \alpha_1 - \alpha_2 \end{aligned}$$

must be recognised as conditions of equilibrium.

The first condition must obviously be always observed as otherwise there would take place a perpetual distillation. The second is a natural consequence of it, and the fact that the experimental evidence indicates a full agreement between the two, appears to be the proof that the ideal gas laws hold true in such cases. If we make use of the evidence as to the molecular state just derived from other data, everything appears in strict agreement with the ideal laws. *I therefore conclude that in most cases the other factors, which might disturb, these laws, do not come into play at all.*

If such was the case, one might expect the law:

$$\alpha_{12} = \alpha_1 - \alpha_2$$

not to be true.

As regards the causes of deviations from the ideal gas laws, many authors have already expressed the opinion that they may be due to the want of exact knowledge of the number of molecules in a given volume. If the actual number of them was known to us, these laws would show themselves valid. The above evidence seems to corroborate this view. In other words these deviations are not due to molecular forces at all. The systems discussed in this paper are far from being ideal, and yet they are in strict agreement with the simple gas laws. The confirmation of this view I can see also in the following facts. The two liquid layers in equilibrium always have the same freezing point. Amongst systems I investigated there were some in which the surface tension of both layers differed enormously. In some other cases the both layers had very nearly equal surface tensions. In both cases, however, the freezing point of the two superposed solutions was the same. If the molecular forces affected the freezing point, this might be different.

Experience has convinced me that the apparent departures from the law of difference can be attributed to some special factors which may disturb the state of equilibrium. In this paper I leave such cases quite out of my consideration, and discuss them elsewhere.¹

The main object of this chapter is to show that the two solutions forming the two superposed layers in equilibrium are equimolecular, i.e. they contain the same numbers of molecules per unit volume.

This means that on addition of one of the components, the molecules added combine with some molecules in solution without increasing their number.

This also means that if in one layer the average molecular weight of the dissolved substance is A, a number of these molecules will combine with one another to form the molecules of the other layers. This can be expressed by the equation:

$$nA = A_n,$$

where "n" is the factor of association. The actual value of A may not be known,² and it may be difficult to determine the same for the want of a suitable method. This, however, is of no importance to us.

We went into all these details because these systems bear an intimate analogy with systems liquid-vapour, where the same phenomena take place *according to precisely the same laws, only without the solvent, which is replaced, so to say, by the vacuum.* In these systems, A represents nothing else but the molecular weight of the vapour, which can be determined by the known method.

¹ Loc. cit.

² Owing to phenomenon of solvation A may comprise some particles of the solvent. Apart from this the solvent retains properties of pure solvent.

IV. SYSTEMS LIQUID-VAPOUR.

Investigation of critical phenomena shows that there is a marked analogy between systems separating into two liquid layers and cases when a pure substance separates into a liquid and vapour at its critical point.

It was pointed out by van't Hoff that in solutions the dissolved matter very often behaves in such a manner, as if it were in a gaseous state; in other words, in this condition it obeys ordinary gas laws.

Thus, it can be shown that in some cases a substance can undergo a process of condensation within a solvent in the same manner, as an individual substance condenses in a space not otherwise filled at its critical point.

The study of systems separating into two liquid layers presents the advantage that the experimental work is easier and one can apply a number of methods for their investigation, which are not applicable for systems liquid-vapour.

Two liquid layers in equilibrium are iso-osmotic solutions as van't Hoff would call them. I use this expression to convey the idea that these solutions being in equilibrium, exercise the same pressure on one another.

It was shown on p. 2412 that in case of partially miscible liquids one of them distributes itself in the other and forms lower or upper layer according as to it is specifically lighter or heavier than the other. Thus, we have such a picture before us, as if liquid and its vapour were incorporated into a solvent, conserving their characteristic properties. It thus appears that, in a sense, the solvent plays the rôle of "vacuum."

The van't Hoff's law says:

The iso-osmotic solutions contain at a given temperature, in the same volume, the same number of dissolved molecules, and this number is the same as if the dissolved matter was gaseous.

From the above analogy it follows that liquid and vapour in equilibrium contain an equal number of molecules per unit volume. This must be always true for systems in equilibrium and they need not be ideal at all, just as it was stated on p. 2415 for systems liquid-liquid.

Vapour and liquid are also iso-osmotic, in the sense that they exercise the same pressure on one another. It is not possible in this case to make use of the freezing point method, as it was done for the systems liquid-liquid. By investigation of the latter systems one can see that the systems liquid-vapour are really the same thing, only without the solvent, which only plays the rôle of a medium in which the system is distributed.

The same can be also made clear from surface tension consideration, although here again we are restricted in the use of methods for systems liquid-vapour. But the investigation of two liquid layers in the vicinity of the critical point explains everything.¹ At the critical point these systems separate into two liquid layers of equal volume, the surface of separation being flat. About 2°-3° below the critical point, it still remains flat, and there is no capillary rise in this region. The two liquid layers formed can be easily separated from

¹ Antonoff: J. Chim. phys., 5, 364 (1907).

one another and it can be shown by capillary method that they have the same surface tension in the critical region, i.e. in the notation as before,

$$\alpha_1 = \alpha_2.$$

This is quite natural as in the critical region, i.e. all round the critical point, the surface tension does not vary with concentration.

The fact that there is no capillary rise at the interface between the two liquid layers in the vicinity of the critical point shows that in this region the interfacial tension $\alpha_{12} = 0$.

In other words: $\alpha_{12} = \alpha_1 - \alpha_2 = 0$.

which is nothing else but a particular case of (4) the law of difference.

In the systems liquid vapour, we can observe the same characteristics in the critical region,¹ viz. the meniscus is flat, and there is no capillary rise. The flat meniscus means $\alpha_1 = \alpha_2$ where α_1 is the surface tension of the vapour and α_2 that of the liquid.

The want of capillary rise means $\alpha_{12} = 0$, where α_{12} is the interfacial tension at the interface liquid-vapour, which is usually measured by capillary method, and commonly called the surface-tension. α_1 and α_2 cannot be measured for the want of method, but owing to their equality, one can conclude that equation (4) can be also established in this case, in the form:

$$\alpha_{12} = \alpha_1 - \alpha_2 = 0.$$

which is valid for the critical region.

One can thus conclude that this equation being particular form of (4), p. 2413, that at least in the critical region *gas and liquid are equimolecular*, as the relation (4) was established subject to that condition. The fact that the above law verifies itself for systems liquid-vapour as well, indicates that the surface tension of the solvent contributes as much to the surface tension of one layer as the other. This follows also from considerations of p. 2410 and justifies the assumption made there. To this case is applicable the same investigation only K, α and p with indices or without will represent corresponding values for pure substances and not solutions. The experimental methods do not allow us to go any further. For systems liquid-liquid, these properties can be studied not only in the critical region, but at temperatures well beyond it, and the remarkable analogy between these phenomena constitutes here again the proof that all above conclusions can be also applied to systems liquid-vapour. It was shown by myself that the law of difference (4) can be extended to systems liquid-vapour already sometime ago² and nowadays this is being realised also by some other authors.³

It will be seen later on that there exist other evidence indicating that systems liquid-vapour are governed by the same laws as the systems liquid-

¹ Wolf: Ann. Chim. Phys. (3) 49, 270 (1857); Drion: (3) 56, 221 (1859); Clark: Phil. Mag. (5) 10, 145 (1880).

² Antonoff: Phil. Mag., 1, 1121 (1926).

³ J. L. Shereshefsky: J. Phys. Chem., 35, 1712 (1931); N. Barbulescu: Physik. Z., 31, 48 (1930).

liquid. See below. Now, I want to point out the importance of the conclusion we arrived at, viz. that vapour and liquid are equimolecular. This gives us a rational method of establishing the molecular weight of the liquid.

The molecular weight of the vapour can be found from its density. If the liquid contains the same number of molecules per unit volume, its molecular weight M_l can be deduced from that of the vapour M_v in the following way:

$$M_l = \frac{M_v \delta_l}{\delta_v},$$

where δ_l is the density of liquid and δ_v that of vapour.

The ratio of these two is nothing else but the factor of association, showing how many simple gaseous molecules form one molecule of a liquid.

The above relation indicates that the molecular weight of a liquid must be variable with temperature. Investigation of these effects requires careful consideration and before proceeding with the question of molecular weight, I shall consider in detail the effect of temperature on properties of liquids.

V. EFFECT OF TEMPERATURE ON PROPERTIES OF LIQUIDS AND VAPOURS AND THE LAW OF RECTILINEAR DIAMETER.

When investigating the properties of liquids and their vapours as a function of temperature, one often gets difficulties due to phenomena of supersaturation: the liquid may not evaporate, or a vapour may not condense at temperatures at which these phenomena are due. From this point of view the systems liquid-liquid present the great advantage because these phenomena never take place, and condensation or the inverse takes place sharply at a determined temperature. This is not difficult to understand. Vapours require a presence of a liquid to do away with supersaturation. When the condensation takes place within another liquid, the latter being a liquid, the condensation or the inverse process always takes place without a lag.

This is important to note in considering the properties as a function of temperature, which are subject to the same laws in systems liquid-liquid and liquid-vapour. For this reason, I prefer to consider the properties of systems liquid-liquid in the first place. A very convenient object for this kind of work is, for example, the system aniline-amylene (trimethyl-ethylene), which has its critical temperature of solution at about 14°C. I determined its so-called solubility curve in such a way that solutions of different concentration were subjected to different temperatures at which they separate into two liquid phases, if they were homogeneous before, or vice-versa. This "clouding temperature" can be observed very sharply especially in the vicinity of the critical point, where two phases are of nearly equal volume, and the separation appears in form of a very thick milk. Thus, in the vicinity of the critical point, every observation can be reproduced several times with a marked accuracy, and with always concordant result. By plotting the concentrations against the temperatures (clouding temperature) one gets a curve having appearance of an assymmetric parabola.

When I did this experiment for the first time, I found that in some places the observations fell off the smooth curve quite appreciably. Thus, for example in some observations in the critical region, where the separation into two layers is very sharp and the temperature can be read off up to 0.01°C . easily, some of the points fell off the smooth curve as much as about 0.5°C . I did not have any idea whatever as to what these phenomena could be due to, and there was a general tendency to attribute these deviations from the smooth curve to experimental errors or to a bad work rather than to intrinsic causes.

At the same time, quite incidentally I had an opportunity of plotting the figures for latent heats of vaporisation of pure liquids, against temperatures, figures which I found in the literature, and which showed at more or less regular intervals quite distinct signs of discontinuity, i.e. there could be observed at some parts of the curve some kinks, Fig. 7, just as I observed them in the solubility curve as mentioned above.

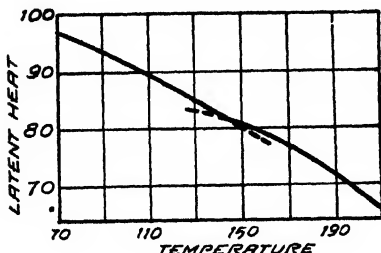


Fig. 7

Having begun to realise that these effects are well above the limits of experimental errors, I repeated twice more the experiments with aniline-amylene.

It is true that the absolute figures found with each sample of amylene were different. Amylene is not a very well defined substance, consisting in varying proportions of several isomers according to the mode of preparation and purification. But in all cases, I found the kinks in the curve, and one of them particularly well pronounced was situated in the vicinity of the critical point.

But if one plots densities of solutions against temperature, one also gets curve having the shape of an asymmetric parabola, but it appears practically smooth. A much greater accuracy is necessary to see whether there are also kinks in this curve or not. It may be that in this latter case these phenomena are masked by a kind of compensation. This becomes clear if one plots the densities against concentrations, this curve having a very peculiar shape.¹ Knowing the limits of experimental error and the accuracy of my observations, I can see that these discontinuities are an intrinsic property of matter.

In the system phenol-water, the same phenomena of discontinuity can be observed very clearly. Phenol is a substance chemically well defined, capable of being obtained in a state of extreme purity.

If we examine figures for other systems found by other authors, it can be seen that practically all of them may be shown to exhibit one or several kinks. The examples of such data are quite numerous, and can be found, for example, in the Landolt-Börnstein Tables.

I noticed long ago that in the data for latent heat of vaporisation for pure liquids, the same phenomena are observed. This I observed at first in figures which were already in existence some 30 years ago or even more. Investigating

¹ Antonoff: *Phil. Mag.*, **1**, 1127 (1926).

other data, which have become known in the course of time, one can notice exactly the same, and this applies to figures of different authors.

These data are not due to direct observations of latent heats of vaporisation, but are calculated on a basis of a certain theory, from densities. It is known that densities can be measured with considerable accuracy, and it is therefore interesting to see whether the density-temperature curves reveal anything of the same kind.

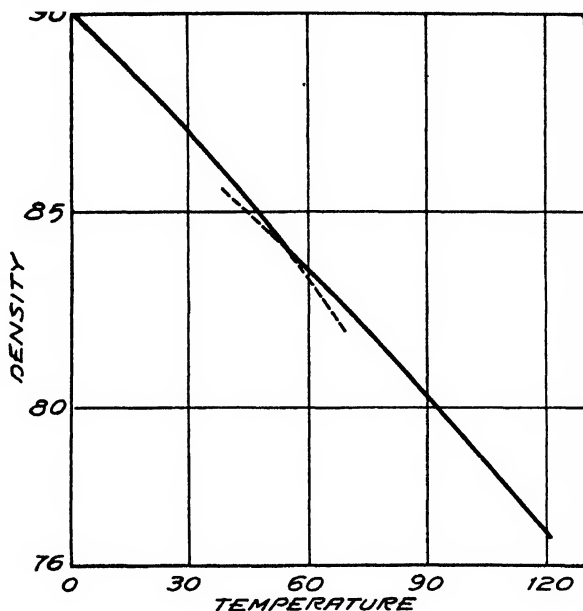


FIG. 8

These discontinuities as a matter of fact can be seen if the densities are given with three decimal places. The existing figures are generally given with four decimals, the last being doubtful.

The density-temperature curves have the kinks not quite so well pronounced as in latent heat of vaporisation curves. This is due to the nature of the relation,¹ whereby these effects are accentuated, but these kinks correspond to the same temperatures in both curves.

The density curves plotted on a millimeter paper on such a scale that one-tenth of a mm. corresponds to a unit in a fourth decimal place, show in some cases the kinks sufficiently clearly that they can be well noticed, as can be seen from one of the adjoining curves, Fig. 8.

It is, however, much better to demonstrate these phenomena mathematically, the method showing itself much more sensitive.

To represent graphically, it is better to take either the sum of densities of the liquid (δ_l) and that of the vapour (δ_v), or their difference. The nature of

¹ The latent heats L were calculated by the formula of J. E. Mills:

$$L = K(\sqrt[4]{\delta_l} - \sqrt[4]{\delta_v}).$$

these relations is such that in the first case we get a rectilinear curve as the two curvatures compensate each other in this case. Whereas, if we take the difference $\delta_1 - \delta_v$, and plot it against temperatures, the curvature becomes much more pronounced. Just if we plot the difference $\delta_1 - \delta_v$, which I shall denote hereinafter with the letter δ without an index, the whole curve for δ beginning from the critical point can be expressed as a series of exponential equations, such as:

$$\begin{aligned} Ae^{\lambda\delta} &= T + A, \\ A_1e^{\lambda_1\delta} &= T + B_1, \\ A_2e^{\lambda_2\delta} &= T + B_2, \\ &\text{etc. . . .} \end{aligned}$$

And this is the most convenient form for treating the subject mathematically. In these notations T is the temperature counted from the critical point as 0, downwards, A , A_1 , A_2 , etc., λ , λ_1 , λ_2 , etc., B_1 , B_2 , etc., are constants characteristic for the equation between two kinks. Thus, the nature of the relationship remains the same for all ranges of temperature, the constants varying only, and changing brusksly when a new portion of the curve begins after a kink.

The first equation naturally differs in such a manner that it contains two identical constants A and A , as δ must become = 0 at the critical point.

To calculate individual values of δ_1 and δ_v one can take advantage of the fact that $(\delta_1 + \delta_v)/2$ is a straight line in the intervals of the curve between two kinks. This expression is known under the name of rectilinear diameter of Cailletet-Mathias. This, however, is a straight line, only between two kinks, and it has a character of a zig-zag line on the whole. Thus one can put:

$$\frac{\delta_1 + \delta_v}{2} = \frac{T + a}{b}, \quad (1)$$

where a and b are constants.

On the other side, the exponential equations as above can be represented as:

$$\delta = \delta_1 - \delta_v = \frac{\log. \left(\frac{T + B}{A} \right)}{0.4343\lambda}. \quad (2)$$

From these two equations values of δ_1 and δ_v for a given interval between two kinks can be calculated, viz.:

$$\delta_1 = \frac{T + b}{a} + \frac{1}{2} \frac{\log. \left(\frac{T + B}{A} \right)}{0.4343\lambda}, \quad (3)$$

$$\delta_v = \frac{T + b}{a} - \frac{1}{2} \frac{\log. \left(\frac{T + B}{A} \right)}{0.4343\lambda}. \quad (4)$$

The two expressions differ only in so far as the logarithmic term comes in with the opposite sign. Thus, in the expression for $\delta_1 + \delta_v$, the logarithmic terms disappear, and the remaining expression is that of a straight line. On

the contrary, in the expression $\delta_l - \delta_v$, the two halves of the logarithmic term add up, and the discontinuity is of a much more pronounced character and is much better visible on a drawing than when δ_l and δ_v are plotted themselves.

Thus, for example, for hexamethylene between 280°C. (its critical point) and 0°, the equations giving accurate values of δ are as follows:

(1) $0,027 e^{20.97\delta} = T + 0,027$	274—280°
(2) $2,328 e^{6.961\delta} = T + 5,20$	260—274°
(3) $7,591 e^{4.743\delta} = T + 18,71$	190—250°
(4) $18,20 e^{3.665\delta} = T + 52,93$	120—180°
(5) $25,03 e^{3.351\delta} = T + 77,31$	60—110°
(6) $66,30 e^{8.258\delta} = T + 1000.1$	0—500°

In the column on the right hand side are given the approximate intervals of temperature between which the given equations are valid. See also Table I on p. 2427.

The kinks can be seen fairly well on a drawing, Fig. 12. The deviations from the smooth curve due to experimental errors are not visible to the eye as a rule, the accuracy of the measurements being well above. Thus each portion of the curve between two kinks appears quite smooth. This together with the fact that *the constants of the equations are so distinct for each portion* is the best proof that these kinks are real and not due to experimental errors.

Similar equations can be deduced for any other substance, whether "normal" or "associated" in the sense in which these words are nowadays used. Thus, the same result is obtained whether the substance contains the group OH or not. The form of relationship remains the same at all intervals of temperature, and so far I know one case only when it does not hold true, is the case of water at about 4°C.

All these facts can be interpreted only in one way, viz. all liquids must be associated and their degree of association must vary with temperature. Effectively, if it were not the case, or if the degree of association did not vary with temperature, one would expect a different type of relationship. One would expect perhaps a linear form of relationship, but the very fact that it is a case of an exponential equation, suggests that there must be here involved some molecular changes.

At the critical point $\delta_l = \delta_v$, the liquid and vapour, both, contain an equal number of molecules per unit volume, i.e.:

$$\delta = \delta_l - \delta_v = 0.$$

It is δ , i.e. the excess density of the liquid compared with that of vapour, which follows the exponential law as a function of temperature. It is interesting to deduce this relation theoretically.

The quantity δ and its variation with temperature must be intimately connected with the formation of complex molecules. Let us call m the number of complex molecules per unit volume, and let us assume that $d\delta/dT$ is proportional to the rate of formation of complex molecules, i.e.

$$\frac{d\delta}{dT} = K \frac{dm}{dT}.$$

The law connecting m with temperature must be of the form

$$\begin{aligned}\frac{dm}{dT} &= \frac{K}{T+B}, \\ d\delta &= \frac{KdT}{T+B} = Kd\ln(T+B), \\ \delta + e &= K \ln(T+B).\end{aligned}$$

By putting $K = I/\lambda$ this expression can be presented in the form:

$$A e^{\lambda\delta} = T + B. \quad (5)$$

The expression thus deduced is identical with the expression found empirically on a basis of experimental data.

It is not difficult now to imagine the whole mechanism of these transformations. Consider a unit volume of the saturated vapour (A) and a unit volume of the liquid (B). Both will contain an equal number of molecules per unit volume, as it follows from this theory. Let us now cool the system down.

The density of A will diminish owing to the loss of a certain number of molecules, say n , which will depart owing to condensation. At the same time the molecules will concentrate themselves owing to thermal effect, assuming that contraction is a linear function of temperature.

On the other side, in the volume B the liquid will become denser because its number of molecules had to diminish by n , in this case, not through departure, but owing to association. At the same time, the system contracted according to a linear law.

Thus, in accordance with this theory both liquid and vapour remain equimolecular in spite of the changed temperature. This picture is in good agreement with equations (3) and (4) deduced empirically (p. 2422). Thus, it becomes clear why the average density $\delta_l + \delta_v/2$ is a linear function of temperature, i.e.

$$\frac{\delta_l + \delta_v}{2} = \frac{T + a}{b}. \quad (6)$$

On the other hand, we have deduced (5) which together with (6) will give equation (3) and (4). This is what one may call the theory of rectilinear diameter. Up to now there did not exist any theory of it at all.

Between two kinks, the above equations give an accurate expression of existing facts. The part of the straight line between two kinks intersect each other sometimes at a quite appreciable angle, which may serve as a method of locating the kinks, see Fig. 9.

The discontinuous character can be also seen in other properties of liquids, but it can be attributed in most cases to density measurements, as the same comes as a factor in calculating these properties. Thus the same character can be observed also in latent heats of vaporisation, viscosities and surface tensions.

The latent heat of vaporisation (L) follows the law of the same form as above, i.e.:

$$C e^{\mu L} = T + D,$$

whereas viscosities and surface tensions can be expressed by a formula containing the temperature in the exponential, i.e. $\alpha + B = A e^{\lambda T}$, where α is the surface tension, which formula is an accurate expression with given constants for an interval of temperature between two kinks. For example, for

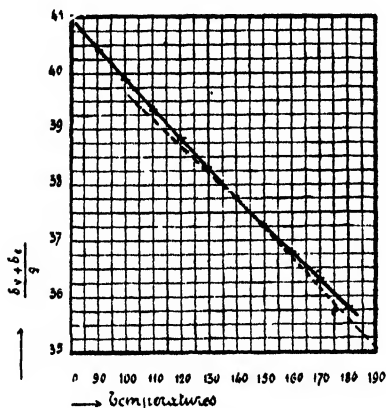


FIG. 9

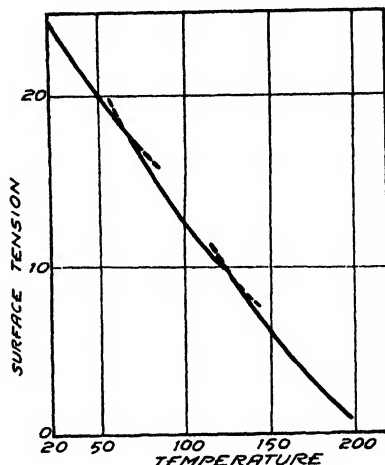


FIG. 10

ethyl acetate this formula acquires the form $\alpha + 33.62 = 33.19e^{.0024T}$ for the interval of temperature 150-110 T approximately, and

$$\alpha + 21.32 = 20.93e^{.0035T}$$

for the interval 100-70 T.

Similarly for viscosities (η) the expression $\eta + c = De^{\mu}$ can be shown to be true.

Curve (Fig. 10) is an example of a surface-tension curve as function of temperature. This is generally believed to be a straight line. Considering the drawing and examples of calculated values, I ask myself, *how can such curves be mistaken for a straight line?*

It is an obvious mistake to draw a continuous curve on a basis of experimental data such as they are. In such case, the deviations from the smooth curve are of a systematic character. The experimental points appear periodically below and above the smooth curve and these deviations are far too large to be regarded as due to experimental errors.

If one calculates by the formulae given by myself, one can see at once that the true law has been guessed, and such deviations that may take place between the calculated values and experimental are obviously due to experimental errors, but they are very small and practically not visible on the curves of the size indicated here.

Apart from all evidence presented hereinbefore, the most striking proof and demonstration of these phenomena lies in the constants of the equations given on p. 2423. They are so distinctly different for every subsequent change that the discontinuous character of the properties in question appears beyond all doubt.¹

VI. MOLECULAR WEIGHT IN THE LIQUID STATE AND ITS VARIATION WITH THE TEMPERATURE

It was shown on p. 2419 that the molecular weight (M_l) of a liquid can be deduced from that of the vapour (M_v) if the latter is known, by the following relation: $M_l/M_v = \delta_l/\delta_v$, where d_l and d_v are the densities of liquid and vapour. This ratio is nothing else but a factor of association, showing how many gaseous particles form one particle of the liquid. Let us call it X .

Thus, $X = M_l/M_v = \delta_l/\delta_v$.

From what we saw in the last chapter, X must vary with temperature.

By plotting X against the temperature one can find its value corresponding to the kinks. It is convenient to find the kinks from the δ curve because the form of the curve is exponential, which makes the calculations easy, and also in the δ curve the kinks are much more visible, than either in δ_l or δ_v curves, as it was already explained before. It is also possible to use the latent heats of vaporisation, which amounts to the same as they are calculated from densities.

This work is laborious and has to be done on a sufficiently large scale to make the kinks visible.

This is illustrated in Table I (giving some numerical data for hexamethylene). In column 1, T represents the temperatures counted from the critical point as zero; in column 2, \sqrt{t} — the temperature in the centigrade scale. In columns 2 and 3, δ_v and δ_l are the densities of vapour and liquid borrowed from the paper of Sydney Young.² In column 6, δ exp. are values obtained as a difference between δ_l and δ_v . In column 7 δ calc. are the values calculated by the equations mentioned on p. 2423 whose numbers are given in column 9. Column 8 shows the difference between δ exp. and δ calc.

The horizontal lines in the table separate figures between which a kink is situated and give thus the rough indication of its position. In some places figures are found between two horizontal lines. This is done in cases where, apparently owing to interpolation, the figures do not fit the curves on either side.³ It is obvious that near the kinks interpolation is not safe. It is seen from columns 6 and 7 that the agreement between experimental values of δ and calculated, is in most cases very good.

Although the kinks in some cases may not be well visible to the eye on the drawing, they are well perceptible to the calculus. I can always base the

¹ Further details can be found in my paper Phil. Mag., 1, 265 (1925).

² loc. cit.

³ These facts were taken into consideration in drawing the curve Fig. 12, where the position of kinks is roughly indicated in accordance with Table I.

TABLE I

1 T	2 t	3 δ_1	4 δ_v	5 δ_1/δ_v	6 $\delta_{\text{exp.}}$	7 $\delta_{\text{calc.}}$	8 diff.	9 Formula
280	0	.79675	0.00014		0.7966	0.7967	+0.0001	
270	10	.7874	.0002		.7872	.7872		
260	20	.7779	.0003		.7776	.7777	+0.0001	(6)
250	30	.7685	.0005		.7680	.7680		
240	40	.7591	.0007	1084	.7584	.7583	-0.0001	
230	50	.7496	.0011	681	.7485	.7485		
225				576				
220	60	.7400	.0016	462	.7384	.7384		
210	70	.7306	.0022	332	.7284	.7283	-0.0001	
200	80	.7206	.0029		.7177	.7177		
190	90	.7106	.0038		.7068	.7067	-0.0001	(5)
180	100	.7003	.0049	143	.6954	.6954		
170	110	.6898	.0063	109	.6835	.6835		
165				96.0				
160	120	.6791	.0082	82.8	.6711	.6711		
150	130	.6680	.0099	67.5	.6581	.6581		
140	140	.6565	.0123		.6442	.6442		(4)
130	150	.6448	.0151		.6297	.6297		
120	160	.6325	.0182	34.7	.6143	.6143		
110	170	.6200	.0219	28.3	.5981	.5981		
102				24.0				
100	180							
90	190	.5926	.0314	18.9	.5612	.5612		
80	200	.5780	.0374	15.5	.5406	.5407	+0.0001	
70	210	.5626	.0444		.5183	.5183		(3)
60	220	.5456	.0525		.4931	.4931		
50	230	.5271	.0625	8.43	.4646	.4645	-0.0001	
40	240	.5063	.0750	6.67	.4313	.4313		
30	250							
20	260	.4533	.1111	4.15	.3422	.3422		
18				4.00				
15	265	.4354	.1248	3.48	.3106	.3105	-0.0001	
10	270	.4125	.1433	3.01	.2692	.2695	+0.0003	(2)
6	274	.3891	.1634	2.40	.2257	.2257		

equation of a curve on three points situated between two kinks in such a way that the agreement with experimental figures will be perfect. But if one chooses points situated on either side of the kink, no smooth curve will ever agree with experimental figures, and the deviations will have systematic character, which makes quite obvious the existence of the kink.

The figures given in Table I do not indicate the exact position of the kinks. To find the more accurate position of the kink, one can draw two por-

tions of δ curve and find the exact temperature of the kink by interpolation. One can also prolong the range of calculated values of δ beyond the temperature of the kink. From this moment the calculated values begin to depart brusksly from the experimental ones.

This is illustrated by Fig. 11, where (the bottom part) differences are plotted against temperatures, in such a manner that for the temperatures above 100 T the values of δ calc. are equal to δ exp. and their difference = 0. Below 100 T these differences begin to grow systematically. The line drawn on these points crosses the abscissae at about 102 T, which is the temperature

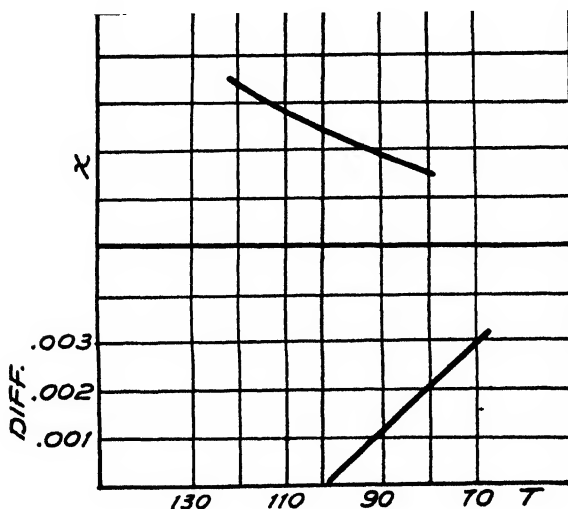


FIG. 11

of the kink. The top part of the drawing shows the values of X plotted against the same temperatures. At 102° the value of X read off the drawing is about 24.

I choose this point because here the data are more reliable. Near the critical point they are not good enough to enable us to say anything definite. It may be that the value of $X = 4$ at 18 T is corresponding to a kink. But it may be that the kink is situated between 40 and 30 T, with the value of $X = 6$.

Although the figures at temperatures further distant from the critical point than 102 T, are most accurate, the determination of X corresponding to a kink becomes more difficult, because dX/dT becomes too large, and a small error in the determination of the temperature of the kink affects X enormously.

Thus I choose as a base the value of $X = 24$ at 102° T. Then, one can observe a value of $X = 96$ at 165 T, which is probably the accurate value, corresponding to the kink, as $24 \times 4 = 96$. Accordingly the table indicates another kink at 225 T with $X = 576 = 96 \times 6$, as the most probable value.

Thus, the process of association of hexamethylene according to this evidence, must consist of the following stages. In the first place, there must be a change (1), not indicated in the table. It commences from the critical point and ends about 3-4 degrees below it, when X passes through the value 2.



About changes of this sort it will be spoken more in detail on p. 2432. Now A_2 either combines as:

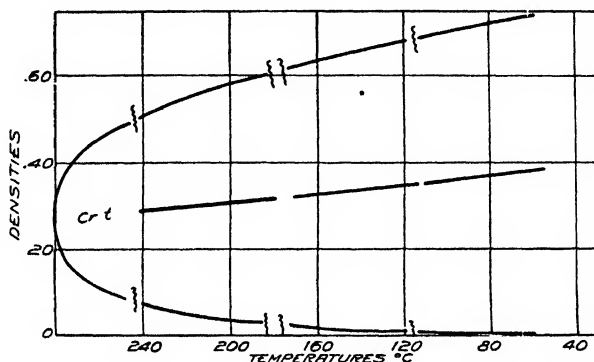


FIG. 12

The following stages will be accordingly



The existing data cannot settle this point with certainty. But this has no effect on further results.

According to the table two more changes can be observed:



In Fig. 12 is given the curve of densities of hexamethylene, the lower branch of the parabola being the densities of vapour, the upper branch is that of the liquid; both meet at the critical point (cr. t. on the drawing). I have indicated the approximate position of kinks, as I have found them mathematically. Near the critical point nothing definite can be seen, the data not being sufficiently accurate, owing to great experimental difficulties. The horizontal line in the middle is the so-called *rectilinear diameter*. For this substance the discontinuities are just above the limit of visibility. One can see from the drawing that the rectilinear diameter is not rectilinear, but is a zig-zag line.

The character of these curves is always the same, and examination of various substances shows that the same phenomena have in some particular

cases much more pronounced features. Several examples, where the kinks are well visible are given in Figs. 7, 8 and 9. Fig. 7 shows a kink in the curve of latent heats of vaporisation. Fig. 8 shows a kink in a density curve for benzine. Fig. 9 gives an example of rectilinear diameter for the same substance, where the angle of intersection of two straight lines is clearly visible. Fig. 10 gives an example of a surface-tension curve of methyl-formate; its discontinuous character is well pronounced.

Sometimes, when the curve is not very well pronounced, I detect the kinks by means of a flexible steel rule. A natural curve can fit well the curved line between two kinks but not otherwise.

It is interesting to mention that in most papers published by the Leiden physical laboratory on this subject, there is a mention of the deviations from the rectilinear diameter and these deviations are stated to be well above the limits of experimental errors, viz. they vary between 0.5 and 2%. It is seen from the above that these deviations are one of the manifestations of the same fact, viz. of the discontinuous character of density curves.¹ I can also give some more examples. Thus for ethyl acetate I found following results. The values of X corresponding to the kinks are as follows:

$$X = 2, 6, 18, 36, 144, 684, \text{etc.} \dots$$

This shows that the process of association consists of a series of consecutive reactions taking place in accordance with the law of multiple proportions.

The individual stages of which can be represented by the following equations: (See also p. 2416).

	Approximate range of temperature
(2) $3 A_2 = A_6$	230°-246°
(3) $3 A_6 = A_{18}$	190°-210°
(4) $2 A_{18} = A_{36}$	150°-180°
(5) $4 A_{36} = A_{144}$	100°-140°
(6) $A_{144} = A_{684}$	50°- 90°
etc. . . .	

Thus, at temperatures corresponding to the kinks, the liquid consists of only one kind of molecules (Molekulgattungen).

For this liquid, the equations for δ were calculated as follows:

$$\begin{aligned}
 (1) \quad & .120 e^{14.98\delta} = T + .120 \\
 (2) \quad & 2.463 e^{5.649\delta} = T + 5.60 \\
 (3) \quad & 5.406 e^{4.360\delta} = T + 12.80 \\
 (4) \quad & 13.39 e^{3.328\delta} = T + 37.64 \\
 (5) \quad & 20.05 e^{2.986\delta} = T + 62.72 \\
 (6) \quad & 94.43 e^{1.754\delta} = T + 228.31 \\
 (7) \quad & 237.1 e^{1.186\delta} = T + 459.65
 \end{aligned}$$

¹ Communications from the Phys. Lab., Univ. of Leiden, Nos. 131, 145, 162, 172, etc.; the details can be also found in my paper, J. Chim. phys., 25, 497 (1928).

In deducing the molecular equations, I omitted the change immediately following the critical point (1) and one corresponding to the low temperature (7). The (1) I omitted because in the vicinity of the critical point special conditions prevail, of which the mention will be made later on. The (7) is left out because the vapour density becomes at room temperatures too low and the results become inaccurate.

By these equations, the δ curve can be constructed for the intervals of temperature roughly indicated on the right hand side. The intersection of two curves on either side of a kink gives value of δ corresponding to a kink at a certain temperature, which can be calculated or read off the drawing. To determine X one can extrapolate the values of δ_1 and δ_v corresponding to the temperature at which the δ curve indicates a kink, and their ratio gives the value of X.

As an example of a liquid called associated, containing OH, I can quote the propyl alcohol for which I found the following changes:

	Intervals of temperature
(2) $6 A_2 = A_{12}$	$250^\circ - 210^\circ$
(3) $3 A_{12} = A_{36}$	$200^\circ - 170^\circ$
(4) $4 A_{36} = A_{144}$	$150^\circ - 130^\circ$
(5) $18 A_{144} = A_{2590}$	$120^\circ - 50^\circ$

The corresponding equations for d being:

$$\begin{aligned}
 (2) \quad & 5.160 e^{4.88\delta} = T + 12.33 \\
 (3) \quad & 11.90 e^{3.787\delta} = T + 34.30 \\
 (4) \quad & .1947 e^{8.788\delta} = T - 47.40 \\
 (5) \quad & 2.744 e^{5.584\delta} = T - 1.30
 \end{aligned}$$

Here again I omit changes (1) and (6) for the same reasons.

It can be seen that the law in this case is just the same as in cases of so-called normal liquids. The only difference which one can notice is perhaps this:

The constants in consecutive changes do not vary in the same regular way, and also the coefficient 18 appears very high. It may be that this irregular character has something to do with the group OH, but at the same time it may be due to some sort of error in experimental results owing to which an intermediate change is overlooked. Such is always possible in some individual cases, as the precision of measurements is not everywhere the same, but even then such omission has no effect on subsequent results. But speaking generally, *I regard these results as beyond all doubts.* Most of these data are borrowed from the work of Sydney Young,¹ whose figures for densities are most probably accurate within less than 0.5%, which accuracy is quite sufficient to warrant the above deductions.

As an illustration of similar behaviour of systems liquid-liquid, I shall give the example of phenol and water, the numerical data being borrowed from the Tables of Landoldt-Börnstein.

¹ Proc. Roy. Dublin Soc., 12, 374 (1910).

In this case, instead of densities, I deal with concentrations and to make the kinks more conspicuous,¹ I plot the excess concentration C ($C = C_2 - C_1$), where C_2 and C_1 are concentrations of two liquid layers in equilibrium, against temperatures calculated from the critical point (i.e. about 80°C .) taken as zero, in degrees centigrade.

Proceeding in the same way as above I determine the temperatures corresponding to the kinks in the C curve, and then interpolate the values of C_1 and C_2 for this temperature.

Thus, assuming that the factor of association

$$X = C_2/C_1$$

I found

$$X = 2, 4, 8 \dots$$

corresponding to the kinks in the curve.

Thus, there is an evidence of two changes

$$(2) \quad 2 A_2 = A_4$$

$$(3) \quad 2 A_4 = A_8.$$

The question now arises when and how the change (1) has arisen, i.e.

$$A + A = A_2.$$

In this case as well as before, I treat this change separately, because in the critical region special conditions prevail, which I shall now discuss more in detail.

It was already mentioned that the change immediately following the critical point is probably of the form $A e^{\lambda\delta} = T + A$, i.e. the constant on both sides is the same. This is necessary to bring δ to zero, when the critical point is reached. I must, however, add that the experimental work in the critical region is very difficult and it has not been sufficiently well investigated.

However, certain evidence indicates that also the nature of the change is somewhat peculiar.

I consider that the above equation is valid within about 3° from the critical point.

If one has three points on this part of the curve, the whole equation can be established and serve for the accurate location of the critical point.

Both phases in the vicinity of the critical point have the same vapour pressure and the same surface tension. This means that separation into two phases in the critical region takes place without an appreciable expenditure of energy.

Independence of these properties² from concentration above the critical point makes me believe that already then the particles of the system combine with one another. Following assumption will be in agreement with the experimental evidence.

¹ See also Phil. Mag., 1, 1129 (1926).

² The curve Fig. 6 is horizontal in the neighborhood of A and B, the points corresponding to two superposed layers in equilibrium. The experiment shows that the curve remains horizontal even above the critical point, where the whole system is homogeneous.

Suppose that $\frac{1}{3}$ of molecules above the critical point combines with another $\frac{1}{3}$. Thus, the number of complex molecules must be equal to the remaining number of simple ones. Above the critical point these molecules are distributed at random. Owing to diminution of kinetic energy, at the critical point and below, the complex molecules begin to settle down, this process of separation taking place without expenditure of energy. The system separates into two phases of equal volume, containing an equal number of molecules per unit volume, according to this theory. Just 2-3 degrees below the critical point, one can generally observe a kink, the ratio of concentrations, resp. densities being two to one.

Thus, the system has given place to a phase consisting of double molecules, by the time the first kink is reached. From this point, a new reaction starts consisting in polymerisation of double molecules, represented by equation

2 $A_2 = A_4$, as in case of phenol-water, or

3 $A_2 = A_6$, as in another example cited above.

And this gives the beginning to what I have called the ordinary changes.

All above is equally applicable to systems liquid-vapour and systems liquid-liquid, so that it is quite unnecessary to treat the two things apart.

The phenomena viewed from the above point are typical phenomena of dissociation (resp. association), the latent heat of vaporisation being nothing else but the heat of dissociation.

VII. SOLID STATE.

If the question of the molecular state of liquids was little advanced hitherto, still less is known about conditions prevailing in the solid state.

If one takes into consideration the evidence provided by the X-ray analysis, the question may even arise, whether one can speak of the molecular weight of a solid at all. If one atom is simply linked with the other, the molecule of it will be as big as the piece of solid we choose to take. In such case the very notion "molecular weight" loses its meaning.

There is, however, sufficient evidence indicating that the atoms in a solid must be also associated into groupings, each group forming, so to say, a unit, representing the smallest mass of a solid, capable of individual existence. One can mention in the first place that W. H. Bragg,¹ as a result of his investigations with X-rays, arrived at the conclusion that the phenomenon of association must also take place in a solid. It is also known that the tensile strength of materials existing is not what it should be in accordance with elementary theories, if it were merely due to cohesive forces acting between individual atoms. Existence of certain groupings might explain this discrepancy.

The chief argument in favour of such view, in my opinion, consists in the behaviour of solids when they are in equilibrium with other phases, namely at the melting point. At this point the solid is in equilibrium with

¹ Loc. cit.

the liquid. The liquid and solid, both are in equilibrium with their common vapour. Thus, if a liquid is associated and its molecular weight is a certain multiple of that of the vapour, the same must be also true for the solid. We saw before that conditions of equilibrium between two phases are:

$$p_1 = p_2 \quad (1)$$

$$\text{and} \quad \alpha_{12} = \alpha_1 - \alpha_2. \quad (2)$$

As far as the first condition is concerned, it is applicable to the solid state as well, at its melting point.

About the second condition, it is difficult to speak with certitude, because it cannot be proved experimentally for the want of methods. I can only say that the tension at the interface solid-liquid at the melting point is generally appreciable, because the meniscus is well curved, indication that the solid has a higher surface tension. As the first (1) condition is necessarily satisfied and the second (2) is only a natural consequence of it, personally I have no doubt whatever, that the law of equilibrium is general for all states, and I therefore believe that the degree of association of the solid at the melting point must be represented by the ratio:

$$X = \delta_s / \delta_v,$$

where X is the factor of association, δ_s density of the solid and δ_v that of vapour.

Judging from the thermal expansion of solids, I conclude that the degree of association of solids does not change, as a rule, with temperature, as it is the case with liquids.

In some individual cases the change in the molecular structure may take place also in a solid, as in the case of tin, which is known to change its structure on cooling. The unit of solid matter thus indicated by this theory may possibly be the actual limit of what the solid matter may attain in a high degree of dispersion.

VIII. GENERAL PRINCIPLE.¹

We have seen that in various instances of systems in equilibrium, such as liquid-liquid, liquid-vapour and liquid-solid, there is one general condition, viz. **the phases in equilibrium exercise the same pressure upon one another, and they are equimolecular, i.e. they contain an equal number of molecules per unit volume.**

I assume that matter in all three states of aggregation is subject to the laws of kinetic theory, only that the mean free path differs widely, and is very small in the solid state compared with the gaseous. The particles having speeds above the average detach themselves from one phase to penetrate into another, where they must, according to my view, regroup themselves. Thus particles of liquid entering into vapour must dissociate and vice-versa.

¹ Antonoff: Réunion internationale de Chim. Phys., Activation et structure des molécules, Paris, 272 (Oct. 1928).

Let us imagine now that the interface between two phases is covered with an impermeable ideal membrane, such that no particles of either kind can go through it. On one side there will be n molecules per unit volumes of one mass, and n molecules of a different mass on the other side. And these both bombarding the membrane from both sides will produce the same pressure.

Imagine now another case. Take two ideal gases occupying equal volume at the same temperature and pressure (case Avogadro). If the two gases are separated by an ideal impermeable membrane, they will be in equilibrium with one another. Without the membrane they will mix together and the analogy with previous cases will disappear. Here again we have n particles of one kind on one side, and n on the other and they produce the same pressure on the membrane. *It is obvious that all systems mentioned are subject to the same law of kinetics.*

Speaking generally, **the systems exercising outwardly the same pressure at the same temperature are equimolecular**, i.e. contain an equal number of molecules per unit volume. This is equally applicable to gaseous matter, liquid or solid. This pressure is equal to the pressure of the gaseous phase, which can be measured in the ordinary way.

Thus, the case Avogadro, in a sense, may be regarded as a particular case of the general principle herein formulated, but it is believed to be accurate in ideal systems, i.e. such where the molecular forces do not come into play.

In this paper it was shown that the phases in equilibrium obey the above law as a result of all internal and external forces. The molecular forces not only have not been neglected, but form the basis of the whole investigation.¹

IX. SUMMARY.

It was established that all systems exercising outwardly the same pressure at the same temperature are equimolecular, irrespective of their state of aggregation.

In particular, two or more phases in thermal equilibrium contain the same number of molecules per unit volume.

Thus, in the case of pure substances the molecular weight of its vapour being known, the degree of association of this substance in another phase can be calculated as a ratio of density of this phase to that of the vapour. In the case of liquids, this ratio X , called the association factor, is:

$$X = \delta_l / \delta_v,$$

where δ_l is the density of liquid and δ_v that of vapour. As the density of vapour diminishes with decrease of temperature, and the density of liquid

¹ This is the point of divergence between this theory and that of J. Duclaux (Loc. cit.); he believes in association, but he does away with molecular forces altogether. Such extreme view has the inconvenience that there is no way of explaining the phenomenon of surface tension, which plays such an important rôle in these matters and which cannot be accounted for without the attractions due to molecular forces. I do not follow either G. G. or N. J. Longinescu (Loc. cit.) who attribute my results to neglect of molecular forces.

increases accordingly, the molecular weight of a liquid attains high values at low temperatures.

These densities vary with temperature in a discontinuous manner, showing kinks at certain intervals.

Between two kinks the curves run according to a definite law, for which there is given an accurate formula. The form of the equation is always the same, only the constants differ for each portion of the curve between two kinks.

At temperatures corresponding to kinks the degree of association, as measured by the above ratio, passes through whole and simple numbers.

The association thus takes place according to the law of multiple proportions, and consists of a number of successive reactions, one reaction beginning when the other is at an end. At the kinks the liquid consists of only one kind of molecules.

At the melting point of a substance, the solid being in equilibrium with its liquid and vapour, the molecular weight of the solid at this temperature can be calculated. There is no evidence of any changes in the solid state comparable with those of the liquid, and the degree of association of a solid appears to remain the same at all temperatures.

STUDIES ON OVERVOLTAGE. V*

A Moving-Coil Oscillograph Commutator System for the Study of Overvoltages and Transfer Resistance¹

BY A. L. FERGUSON AND GRAHAM M. CHEN²

In previous articles³ it was shown that difficulties inherent in the commutator rendered the commutator-potentiometer system undesirable for the measurement of overvoltage and transfer resistance. The present article is a description of a commutator oscillograph system which is much superior for such determinations.

The moving coil oscillograph has been used by Reichinstein,⁴ LeBlanc,⁵ Lattery⁶ and Miller⁷ in studies of transient phenomena at electrode surfaces in electrolytes. In all these cases a source of intermittent direct current was used and the electrodes were connected directly to the oscillograph. The method was finally rejected because the oscillograph drew considerable current for its operation and thus changed the potentials of the electrodes under investigation while those potentials were being measured. This difficulty was partially overcome by Holler⁸ through the use of a vacuum tube amplifier. He used the new arrangement to study polarization and the nature of "transfer resistance" or as he called it "boundary resistance." His oscillograph required 150 milliamperes for full-scale deflection which made it necessary to use a three-tube amplifier. Even then it required 15 millivolts change in grid potential to produce a change of 1 milliamperes through the oscillograph circuit; which means the arrangement is not suitable for accurate work.

The cathode ray oscillograph has been adopted by Newbery⁹ for the study of polarisation and overvoltage. It is ideal in respect to its capacity to accurately follow extremely rapid changes of potential. Vibrations having a frequency of 10^6 per second may be recorded. It is also especially desirable in that it draws practically no current from the source. A marked disadvantage, however, is that it gives a deflection of only one millimeter per volt. By the use of an amplifier it is possible to secure deflection of one millimeter per 100 millivolts. Another very serious difficulty is that the

* Contribution from the Chemical Laboratory of the University of Michigan.

¹ The oscillograph used was purchased from the Faculty Research Fund of the University of Michigan which thus made this work possible.

² The junior author wishes to acknowledge his indebtedness to the China Foundation for the Promotion of Education and Culture for the granting to him of a fellowship which made it possible for him to continue his research work at the University of Michigan.

³ Ferguson and Chen: *J. Phys. Chem.*, **36**, 1156, 1166 (1932).

⁴ Reichinstein: *Trans. Faraday Soc.*, **9**, 228 (1914); *Z. Electrochemie*, **16**, 916 (1910).

⁵ LeBlanc: *Z. physik. Chem.*, **5**, 469 (1890); *Trans. Faraday Soc.*, **9**, 251 (1914).

⁶ Lattery: *Trans. Faraday Soc.*, **19**, 827 (1924).

⁷ Miller: *J. Franklin Inst.*, **19**, 771 (1925).

⁸ *Bur. Standards Sci. Paper*, **20**, 153 (1925).

⁹ *Proc. Roy. Soc.*, **107A**, 487 (1925).

energy of a single discharge of the cathode ray tube is so slight that many discharges are necessary to affect the photographic plate. In fact Newbery found that the plates had to be exposed for 30 sec. while the circuit through his electrode system which was being measured was made and broken about 14 times a second. It is, therefore, a serious question as to how much confidence can be placed in values obtained with such an arrangement. This topic will be discussed more fully later.

The Einthoven string galvanometer has been used by some to record electrode polarisation phenomena. Bowden and Rideal¹⁰ have used it extensively for this purpose. Concerning their work, however, Newbery states that "the maximum frequency of the string galvanometer, which is about 300 per second is far too low, and unreliable results have been obtained by using it for this purpose, as it is quite incapable of following the extremely rapid changes of potential which occur."

In order to determine with a high degree of accuracy whether there is any kind of a surface resistance over which a portion of the applied potential is lost before it reaches the electrode it is necessary to have an instrument: (1) that will give a complete discharge curve from the time of opening the switch; (2) that will show the path of the curve during the first 0.001 second of the discharge interval; (3) that has a sensitivity of about one millimeter per millivolt; (4) that responds instantly to the variation of current through it; and (5) that draws no current from the electrodes under investigation. No apparatus or method thus far described in the literature fulfills these requirements. The present paper is a description of such an apparatus and method.

Apparatus and Material

The oscillograph used was a modification of the two-element Osiso made by Westinghouse Electric Co. The supersensitive element gives one centimeter deflection per milliamper. Energy to operate the element was supplied by a two-tube resistance coupled amplifier. A diagram of the amplifier is given in Fig. 1a. As the first tube, T_1 , a CX₃₂₂ was used, and the second, T_2 , was a power tube CX₃₇₁. R_1 and R_2 represent two noninductive resistances of 850,000 and 50,000 ohms respectively, R_2 being variable. The space charge grid g_1 was maintained positive 4.5 volts with respect to the filament, while the screen grid g_2 was connected to the negative side of the potential under investigation and acted as a control grid. The grid g_3 in the power tube was made 22.5 volts positive to the filament. Two milliammeters, A_1 and A_2 , were employed to measure the filament currents which were held constant by the variable resistances, r_1 and r_2 . The output current from the power tube could be measured by either the ammeter, Am_1 , or the oscillograph, osiso; see Fig. 9b₂.

The amplifier was calibrated by applying known potentials to the grid circuit, and measuring the corresponding plate currents with a milliammeter. The amplification curve, plate current against grid potential is given in Fig. 2.

¹⁰ Proc. Roy. Soc., 120A, 61 (1928).

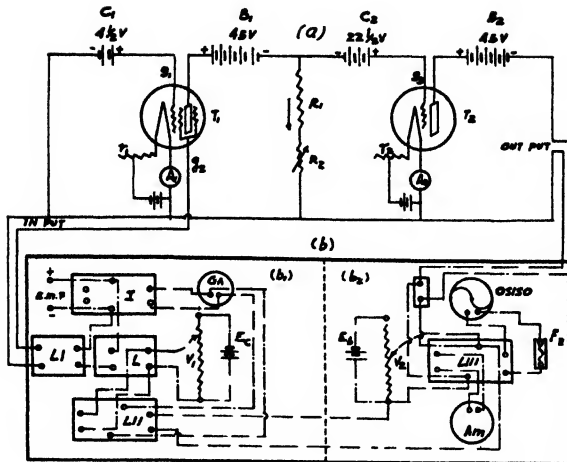


FIG. 1

The amplifier circuits are shown in 1a. The arrangement for connecting the unknown E.M.F. in series with a known potential V_1 , and the resulting potential to the potentiometer or amplifier is shown in 1b₁. The arrangement for connecting the output of the amplifier to either the millimeter or the oscilloscope is shown in 1b₂.

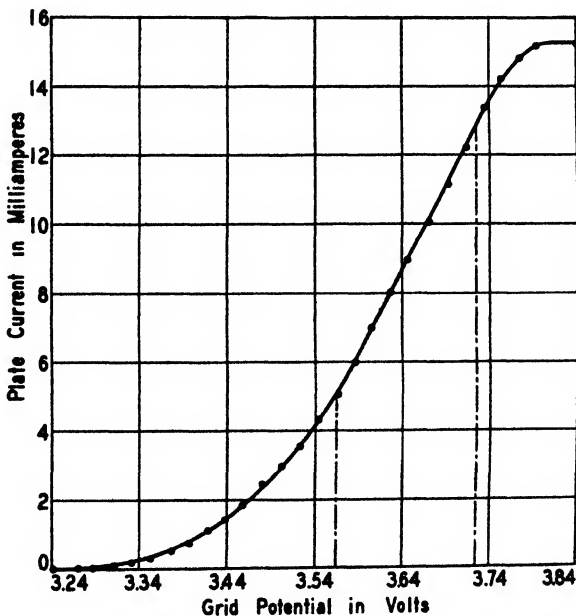


FIG. 2

Calibration curve of amplifier.

For all experiments in the present investigation, the linear portion of the curves used is between the grid potentials, -3.564 and -3.724 volts, as indicated by the distance between the two vertical lines. This difference of potential, 160 m. v., gives rise to a plate current of 7.8 ma.

The polarising current was interrupted intermittently with the direct connected motor driven commutator described in an earlier paper.¹¹

The cell system and the switch board are the same as that described in an earlier article.¹²

The whole set up is a combination of the apparatus employed in the earlier commutator-potentiometer method with the addition of an amplifier and oscillograph. In Fig. 1b₁, the symbol, G.A., for simplicity, represents the entire potentiometer assembly described in the earlier articles. By means of switches I, L, and LI in Fig. 1b₁, the unknown potential, E.M.F., may be measured either by the potentiometer as in the previous work or by the oscillograph. When the potentiometer is used, switch I is closed to the right and the other two are open; when the oscillograph is used, switch I is open and L and LI are closed. By means of the switch LIII a millimeter may be substituted for the oscillograph indicated in Fig. 1b₂ as osiso. The potential divider E_a is used to insert a known voltage V₁ in series with that under investigation in order to control the total potential applied to the grid of the amplifier. Another potential divider E_b is used to insert a known potential V₂ in the plate circuit in order to control the current passing through the oscillograph.

With this apparatus it was possible to measure potential changes of one millivolt and a time interval of 0.0001 second. With slight modification the sensitivity could be increased even more if desired.

Experimental

The manipulation of switches for the various measurements when the oscillograph is used is the same as given in Table I of an earlier article.¹²

By setting the r.p.m. of the commutator at a definite ratio to that of the drum of the oscillograph, any desired number of complete cycles of the charging and discharging curve may be obtained on one film.

The following symbols are used in connection with the various oscillograms.

1. For measurements made by the commutator method.

- A = potential of anode against anode standard.
- A₁ = potential of anode against cathode standard.
- K = potential of cathode against cathode standard.
- K₁ = potential of cathode against anode standard.
- S = potential of anode against cathode.
- I = potential of anode standard against cathode standard.
- Z and Z₁ = zero lines for the two vibrating elements.
- c = the beginning of charge.
- d = the beginning of discharge.

¹¹ Ferguson and Chen: J. Phys. Chem., **36**, 1156 (1932).

¹² Ferguson and Chen: J. Phys. Chem., **36**, 1166 (1932).

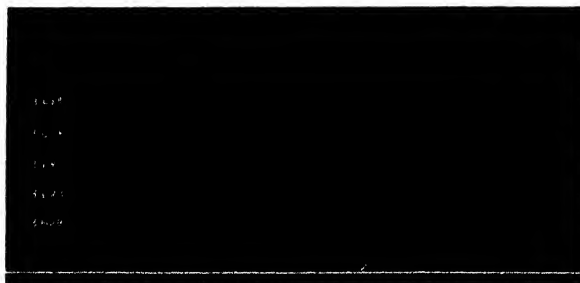


FIG. 3

Calibrated film. The potential used for each line is given at the left end of the line. The zero of the vibrator is indicated by Z' .

2. For measurements made by the direct method.

The same symbols are used as in the commutator method except a prime is added to each.

To calibrate the films, known potentials from a potential divider were measured by the potentiometer system then applied to the amplifier and the resulting plate currents were first measured with a milliammeter then applied to the oscillograph and the steady deflections of the vibrating element recorded as straight lines on the film. Such a calibrated film is shown in Fig. 3. It was necessary, of course, in all of the work to maintain the filament currents for T_1 and T_2 very constant. Frequent recalibrations were made.

Oscillograms were taken by both the commutator and direct methods on the same film and practically simultaneously, using the same voltage V_1 in the grid circuit and the same balancing potential V_2 in the plate circuit.

Data obtained with the commutator and reported earlier¹¹ indicated that one source of discrepancy between the direct and commutator methods is contact resistance of the brushes on the disk, especially at high speeds. This same phenomenon was studied by means of the oscillograph. The results are shown in Fig. 4. The only factor changed to produce the different lines

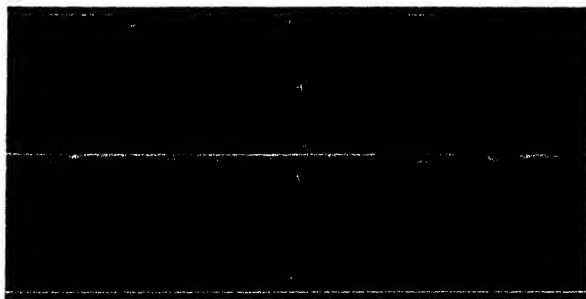


FIG. 4

Single electrode potentials of the anode A' to A'' , and of the cathode K' to K'' obtained by the commutated-direct method at r.p.m.s. from zero to 800.

was the r.p.m. of the commutator. The smooth lines A' and K' represent the anode and cathode potentials respectively with the commutator stationary, which corresponds to the direct method. Lines A'' and K'' represent the potentials at the r.p.m. 800. The lines between A' and K', and A'' and K'' correspond to intermediate r.p.m.s. These oscillograms confirm the earlier conclusions that the electrode potentials decrease with increase in r.p.m. of the commutator due to increase in brush contact resistance. The zigzag nature of the curves is due to variation in contact resistance. The corresponding currents through the polarisation cell were measured, also, at the same time, and the data show a decrease in current with an increase in

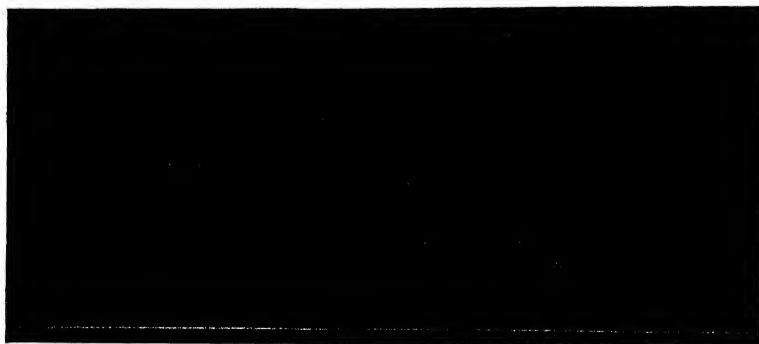


FIG. 5

The curves represent the potentials of the following systems (the numerical values are for the direct method obtained with the potentiometer).

S = potential of anode vs cathode standard. Bottom, 1.847V; top, 2.047V.

A = potential of anode vs anode standard. Bottom, 1.142V; top, 1.275V.

K = potential of cathode vs cathode standard. Bottom, 0.703V; top, 0.735V.

I = potential of anode standard vs cathode standard. Bottom, 0.002, top, 0.039.

c = beginning of charge.

d = beginning of discharge.

r.p.m. for a constant total applied potential; as the r.p.m. increases from 0 to 900 the current decreases from 220 ma. to 120 ma. This decrease is due to an increase in brush contact resistance.

In all measurements made with the oscillograph the I.R. drop through the connecting wires, discussed in an earlier paper, was reduced to a minimum by using heavy leads only six inches long.

Some of the oscillograms obtained with platinized platinum electrodes in 2 N H₂SO₄ are shown in Figs. 5 and 6. A large number of such oscillograms were taken under a variety of conditions particularly for as wide a range of current density as possible and for various speeds of the commutator and the film drum. The two shown here are typical. In these figures curve A shows the change in potential of the anode during charge and discharge; curve K, the change in cathode potential; curve S, the change in total potential across the cell; and I the I.R. drop through the solution between the electrodes.

Curves A and S are strikingly similar to those shown in Figs. 4, 5 and 6 of an earlier article,¹² obtained so laboriously by means of the commutator and potentiometer. These curves furnish strong confirmation of a conclusion drawn on the basis of the earlier work to the effect that potentials measured over the whole or any part of the charge or discharge intervals, as has been done so frequently in the past by other investigators in this field, must be averages and practically meaningless. There are three sets of curves in Figs. 5 and 6; the set at the bottom of Fig. 5 was obtained with a current density of 0.0005 amp.; the set at the top with a current density of 0.0089 amp.; the set in Fig. 6 with 0.0221 amp. The lower part of S in Fig. 6 is

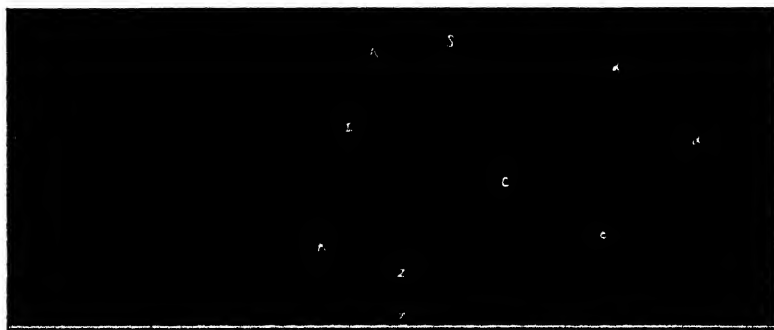


FIG. 6

The curves in this figure are for the same systems as in Fig. 5 except for higher applied potentials. The values by the direct method are: $S = 2.172$, $A = 1.335$, $K = 0.740$, $I = 0.097$, and the polarising current = 0.0221 amp.

missing because the total change in potential across the cell is greater than it is possible to record on the film.

At the bottom of these and all other oscillograms to be given later is represented the curve for a 120 cycle circuit.

It was pointed out in the earlier work (Fig. 5, Ref. 12) that there was an indication that the charging current reached a maximum early in the charge interval then decreased very slowly. There is a slight indication of this same phenomenon in these I curves. This is shown much more conclusively in Fig. 7.

The oscillograph proved to be an excellent means for making a direct comparison of the direct and commutator methods for measuring polarisation. Oscillograms were taken by both methods on the same film and practically at the same time and thus under identical conditions. Typical photographs are given in Figs. 7 and 8. The records of potentials obtained by the direct method appear as straight lines marked A' , K' , I' and S' . The numerical values for these potentials as measured by the potentiometer are given under each figure. The curves obtained by the commutator method are designated in these figures with the respective symbols without the primes.

These curves demonstrate several points. Firstly, the curves for anode potential, A , by the commutator method show maximum values identical

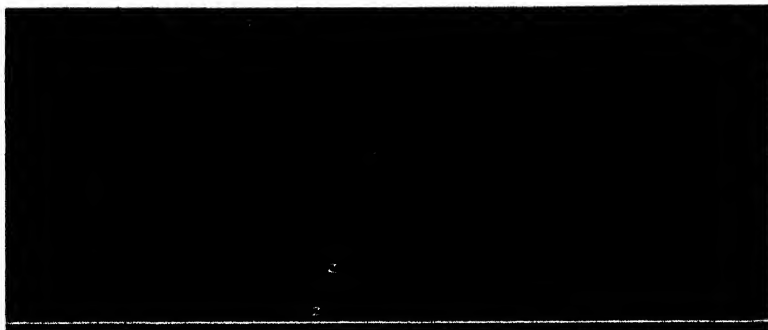


FIG. 7

The curves show the potentials of various systems by both the direct and commutator methods. $A' = 1.335$, $K' = 0.740$, $I' = 0.097$, current = 0.0221 amp.

with the corresponding values, A' , by the direct method. This confirms the statement made by Ferguson and Van Zye¹³ that "the commutator and the direct methods would give the same values if measurements by the commutator method could be made at the instant the polarising current is interrupted." This point of view was greatly strengthened by the work of the present authors¹² with their improved commutator potentiometer; and oscillograms shown here eliminate any question that might have remained. Secondly, the maximum potential of the cathode by the commutator method is always slightly less, for low current densities, than the value given by the direct method. Such a phenomenon was not anticipated, but there is no doubt of its reality. In magnitude the difference amounts to two to five millivolts. This difference can not be due to a transfer resistance since such a resistance would cause a vertical drop at the beginning of discharge and would result in a difference in electrode potential on charge and discharge but could not cause a difference between the maximum value by the commu-

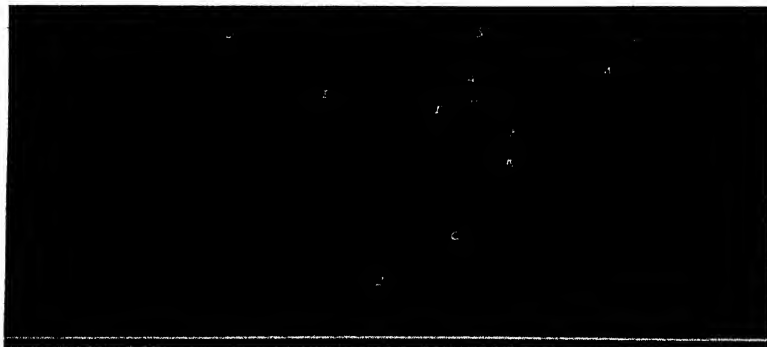


FIG. 8

The curves show the potentials of various systems by both the direct and commutator methods. $S' = 1.289$, $K' = 0.735$, $I' = 0.042$, current = 0.010 amp.

¹³ Ferguson and Van Zye: *Trans. Am. Electrochem. Soc.*, **47**, 227 (1925).

tator method and the value by the direct method as observed here. It should be noted that the total potential, S , across the cell measured by the commutator is less than the value given by the direct method by approximately the same amount as the cathode difference. The S curve is still rising and the probability is that K is also rising and, if sufficient time were allowed, the values by the two methods would become identical. This point of view is supported by other data not given here which show that at higher current densities the curves rise to a maximum much more rapidly and the values by the two methods are identical. There is a slight indication of that in Figs. 7 and 8. At the higher current density used in Fig. 7 the difference between the K and K' curves is less than the difference in Fig. 8 where a smaller current density was used. The S curve could not be shown in Fig. 7 because the change in potential was too great to fit on the film.

Thirdly, these curves show that the current I by the two methods is practically identical. As already pointed out there is a slight tendency for the current by the commutator method to be a little higher than by the direct method during the early part of the charge interval; but it drops off slowly as the charge interval continues. This is clearly evident in Fig. 7. The decrease in I is probably due to the corresponding increase in K .

Fourthly, it is shown that time is required for the electrodes to reach an approximate maximum value. For the current densities of the order used in these experiments, this time is about 0.008 second for the cathode and 0.04 second for the anode. This means that at least that amount of time must be allowed charge and discharge intervals by any method used to compare the commutator and direct methods. Oscillograms not shown here were taken that prove this point.

Fifthly and finally, these curves give no evidence of a vertical drop at the beginning of the discharge intervals such as was found by Holler and Newbery, other than that due to the I . R. drop through the solution. These curves confirm, therefore, all previous work done in this laboratory to the effect that there is no such thing as transfer resistance or any other kind of boundary resistance at the surface of platinized electrodes during the electrolysis of a 2 N solution of sulfuric acid.

Summary

1. An oscillograph-commutator system is described that is very well adapted to the study of transient electrode phenomena.
2. Oscillograms are given showing changes in various potentials during charge and discharge intervals.
3. Oscillograms are given showing a direct comparison of the polarisation potentials as determined by the commutator and direct methods.
4. The work with the oscillograph described in this paper confirms in every respect the work with the commutator-potentiometer system described in earlier papers.

A PHOTOGRAPHIC STUDY OF THE GROWTH OF ELECTROLYTIC STRIATIONS

BY ROBERT TAFT AND OREN R. BINGHAM¹

In a previous paper² we have reported upon the electro-deposition of copper in the presence of gum arabic. In that study the effects of the gum arabic upon the form and mass of the cathode deposit are ascribed to the mutual adsorption of gum arabic and copper oxides upon the surfaces of the newly formed copper crystals. Deposits obtained in those cases where the concentration of gum arabic was high or the hydrolysis of copper sulfate was relatively extensive were very markedly striated.

Such striated deposits have been known for many years, although a satisfactory explanation of their growth has never been made. It has been recognized that the convection currents set up in a "still" electroplating bath, as well as the presence of a foreign substance, were essential for their formation i.e. some material (usually organic in nature) other than the metallic salt and water forming the plating bath. The most serious attempt to explain the formations of such deposits has been that of Rosa, Vinal and McDaniel³ in connection with the striations encountered in the silver coulometer. Their explanation is as follows: the presence of certain types of impurities leads to the reduction of traces of Ag^+ , forming colloidal silver. This colloidal silver finds its way to the cathode and is deposited upon silver crystals growing upon its surface. This deposition of colloidal silver distorts the crystal structure of the growing silver deposit; the deposit now "grows by preference upward in the direction favored by the upward movement of the liquid." These deposits tend to form elongated structures, which in time grow into one another, developing well defined ridges, or striae. In time the striae will disappear by growing into each other laterally.

The data of Marie and Buffat⁴ and of Taft and Messmore⁵ offer a somewhat different explanation of the cause of striations obtained by depositing copper in the presence of gelatin. These authors found that gelatin (or its degradation products) was actually present in the copper deposit, the weight of the deposit being materially enhanced by its presence. Further, it seems fairly well established that the gelatin finds its way into the deposit as a result of adsorption upon the depositing copper crystals. The growth of striations in such solutions has been explained by this assumption, i.e. adsorption of gelatin by copper.⁶

¹ Presented before the Kansas Academy of Science, McPherson, Kansas. April 16, 1932.

² J. Phys. Chem., **36**, 2338 (1932).

³ Bur. Standards Bull., **9**, 263 (1912).

⁴ J. Chim. phys., **24**, 470 (1927).

⁵ J. Phys. Chem., **35**, 2585 (1931).

⁶ Cf. Taft and Messmore: Loc. cit.

In the case of the deposition of copper in the presence of gum arabic under the conditions mentioned in the opening paragraph of this paper, the striations offered such contrast to the base metal as to make it appear feasible to study the growth of such striations photographically. Such a study should furnish information bearing on the cause of the formation of striated deposits as well as furnishing a record of many of the statements already found in the literature concerning their growth, but for which there is no record save description.

Our method for recording the growth of such deposits was to construct a wooden cell, some $4 \times 4\frac{1}{2} \times 6\frac{1}{2}$ cm. in dimensions. One end was fitted with a window made from optical glass and cemented in with de Khotsinsky cement.¹ An anode was made of heavy copper sheet coiled to allow

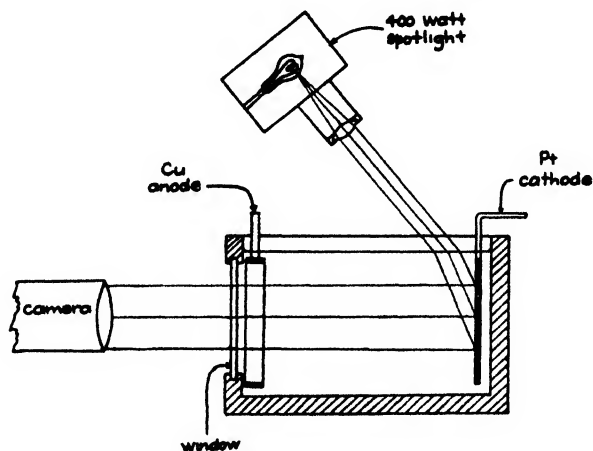
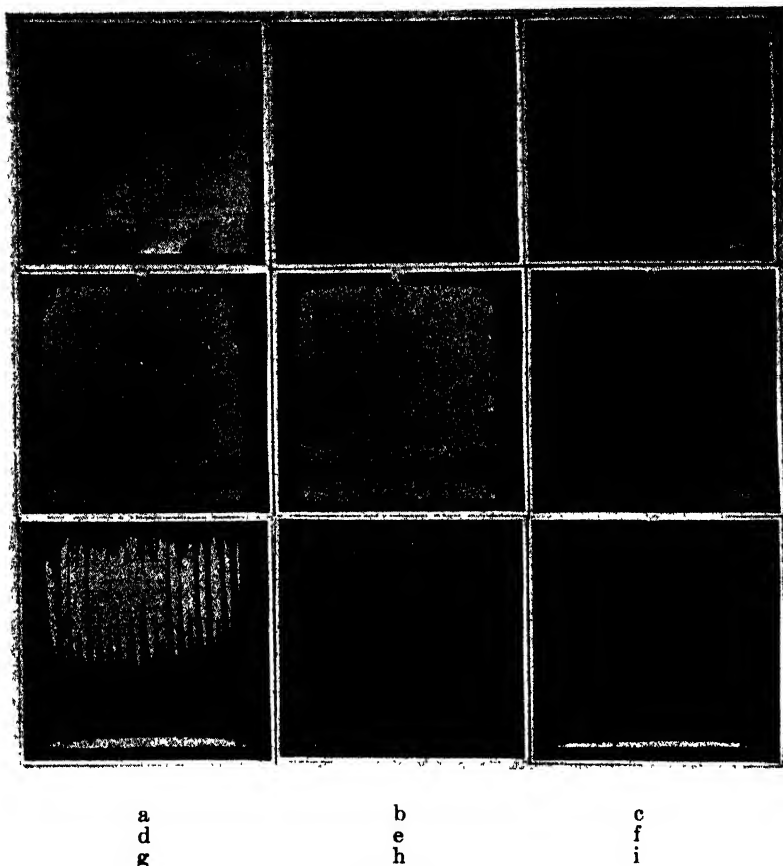


FIG. 1

a clear vision of the far end of the cell through the window. The cathode of platinum (2.5 cm. on a side) was placed at the end opposite the window and was then illuminated from above by a 400 watt focusing spot light. The arrangement is shown diagrammatically in Fig. 1. Powerful illumination was necessary because of the very considerable absorption of light by the electrolyte, copper sulfate. A view camera fitted with a Bausch and Lomb Tessar lens was set up in front of the window and focused upon the cathode. A series of photographs of the cathode was then made as electrolysis continued, without disturbing either the electrolytic cell or the camera. In order to reduce the time necessary for illumination (which would induce local heating) super-speed panchromatic cut film was used as the recording medium, the exposure necessary being 10 seconds at $f\ 16$, with a lens of $7\frac{1}{2}$ " focal length and at bellows extension of 22". Electrolyses were carried out at room temperature, which for the Series 1 photographs was 32°C , and for the Series 2 set was approximately 40°C . The Series 1 photographs were obtained in a solution containing 0.5 M copper sulfate and 1.5 grams of gum

¹ The entire interior of the cell was coated with this cement to render it solution-proof.

arabic per 100 cc. of solution at a current density of 2 amperes per square decimeter. The form of the deposit obtained from zero time up to $2\frac{1}{2}$ hours is shown in Series 1, a to i inclusive.



SERIES I

The growth of the Cathode Deposit in 0.5 M CuSO_4 .

Current Density, 2 amperes per square decimeter; 32°C ; 1.5 grams of gum arabic per 100 cc of solution. The deposit was photographed at the following time intervals: a, 0.0 minutes; b, 5 minutes; c, 25 minutes; d, 40 minutes; e, 50 minutes; f, 60 minutes; g, 1.75 hours; h, 2.25 hours; i, 2.5 hours.

Our explanation of these deposits is as follows: Due to the form of the anode and also to the well-known tendency of current lines to converge on edges, the initial current density will be considerably greater around the edges of the cathode than upon the main face of the cathode. This results in an initial greater deposition of copper around the edges of the cathode, resulting as we have already pointed out¹ in an increasing hydrolysis. As a result of this hydrolysis, cupric hydroxide is formed, which, together with the gum arabic, is adsorbed upon these areas forming a dark-colored deposit. The extent of this process is not great, as the second photograph (Series 1,

¹ Taft and Bingham: Loc. cit.

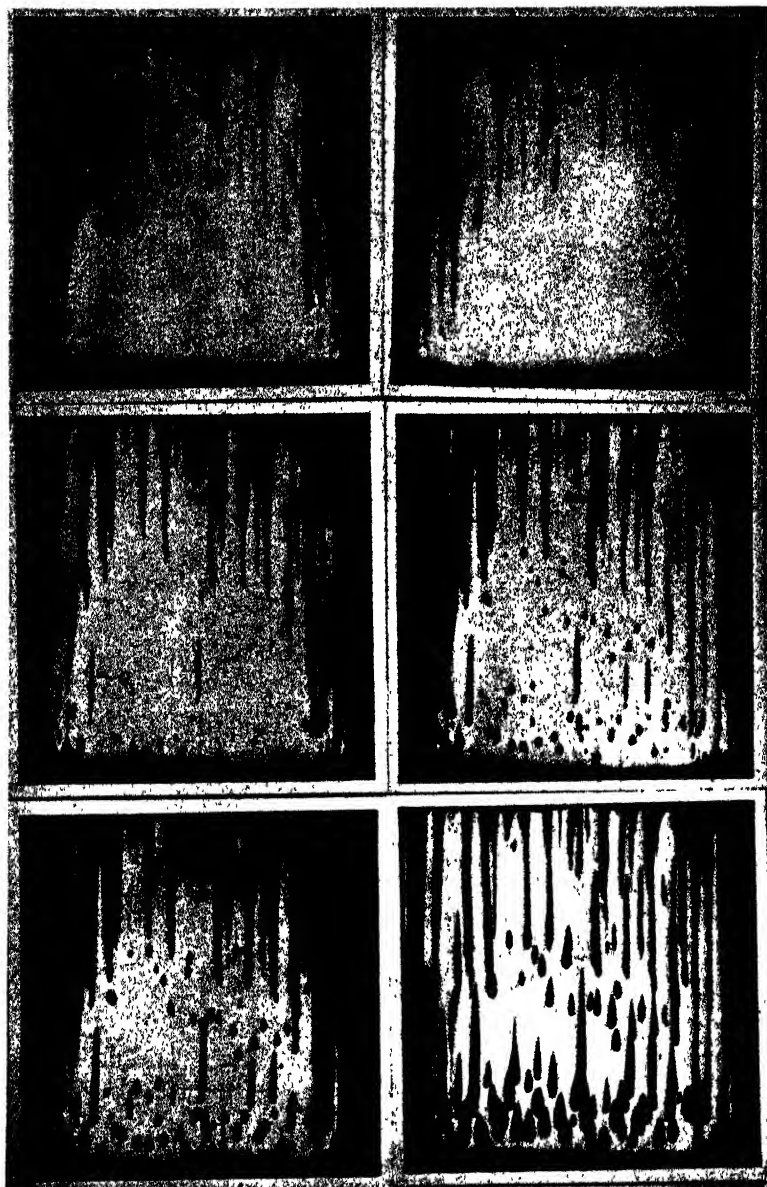
No. b) still shows the scratch marks around the edges of the base metal (compare Series 1, No. a). There is a deposit of dark color around the edges (with the exception of the bottom edge) which apparently prevents, temporarily, the further deposition of copper. It will be shown later in this paper that the addition of gum arabic produces an increase in the cathode polarization which could account for prevention of copper deposition in this area. The increased polarization around the edges diverts the current lines to the face of the cathode where apparently the correct density is quite uniform and copper (the light-colored area) is laid down. (As we have already pointed out, this copper may contain some copper oxides or gum arabic as a result of adsorption). As electrolysis proceeds, however, the solution around the cathode becomes more dilute for two reasons. First, due to the difference in transport number of sulfate and copper ion, there will be a more or less uniform dilution of the electrolyte in this region; second, due to the deposition of copper upon the cathode and the solution of copper at the anode, a well established convection current will be set up, the solution becoming progressively more dilute as it rises up the face of the cathode. As a result of these dilution effects, there will be produced more and more cupric hydroxide. When the concentration of this substance reaches a certain value, it is adsorbed simultaneously with the gum arabic,¹ producing the dark colored area. The formation of this dark-colored area first becomes appreciable in the photograph of Series 1, No. d, although careful examination will show it in Series 1, No. c. Series 1, No. d is produced after some forty minutes of electrolysis. The time at which this phenomenon first became apparent could be reproduced to the minute in duplicate trials. Once it has started, the dark area bridges rapidly across the electrode, at the same time growing upward. The rising electrolyte (after it leaves a given dark area) becomes richer in copper oxide as dilution continues up to a certain value² and poorer in gum arabic, due to its increased adsorption when in the presence of cupric hydroxide. In addition to the dilution of the gum arabic caused by its adsorption there is also a diluting tendency due to the migration of arabate ions³ toward the anode. These two effects are sufficient to prevent further deposition of the dark-colored material until the solution behind the advancing front supplies the necessary gum arabic, which, we must assume, is not extensively adsorbed upon the dark-colored area already laid down.⁴ In this way the dark-colored deposit continues to grow upward, the small initial

¹ As we have pointed out in our first paper, there is apparently a factor similar to a solubility product involved, i.e. when $C_{\text{gum}} \times C_{\text{copper oxide}}$ (C's representing concentrations) exceeds a certain value, the dark-colored area is produced. In fact, the formation of this dark-colored area appears very similar to a supersaturation phenomenon. The original dark areas appear very suddenly and grow quite rapidly during the first interval of their formation, the rate of growth diminishing after the first few areas have been formed.

² It must be remembered that the concentration of cupric oxide (or hydroxide) is the result of two factors, the extent of hydrolysis of the salt and also of its concentration.

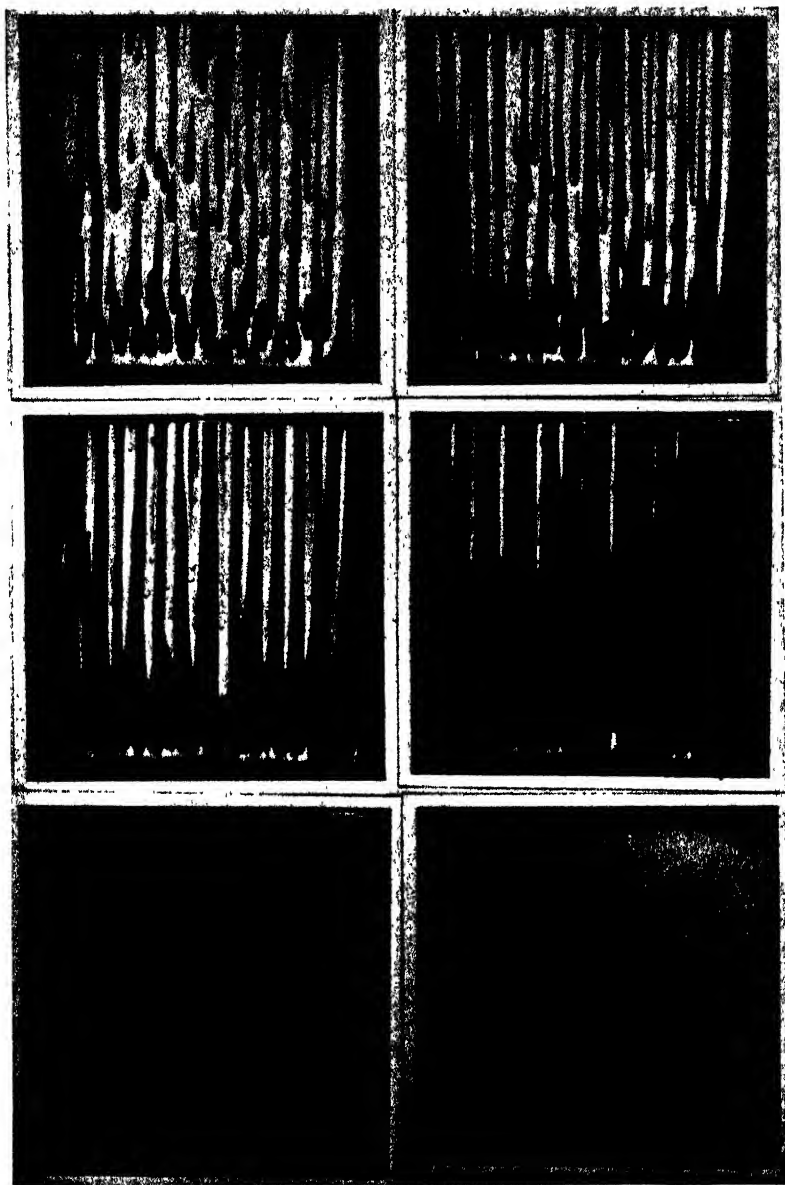
³ Cf. Taft and Malm: J. Phys. Chem., 35, 874 (1931).

⁴ As we have already pointed out, the formation of the dark-colored deposit also likely prevents the deposition of copper in this region, as long as there are any copper areas present. The prevention of copper deposition in this region increases the effective current density in the remaining region.



SERIES 2

The growth of the Cathode Deposit in 1 M CuSO_4 . Current Density, amperes per square decimeter; 40°C ; 1.5 grams of gum arabic per 100 cc. solution. The photographs were taken at the following time intervals: a, 30 seconds; b, 3.5 minutes; c, 15 minutes; d, 20 minutes; e, 25 minutes; f, 45 minutes; g, 60 minutes; h, 1.5 hours; i, 2 hours; j, 3 hours; k, 4 hours; l, 5 hours.



SERIES 2

The growth of the Cathode Deposit in 1 M CuSO_4 . Current Density, 2 amperes per square decimeter; 40°C ; 1.5 grams of gum arabic per 100 cc. solution. The photographs were taken at the following time intervals: a, 30 seconds; b, 3.5 minutes; c, 15 minutes; d, 20 minutes; e, 25 minutes; f, 45 minutes; g, 60 minutes; h, 1.5 hours; i, 2 hours; j, 3 hours; k, 4 hours; l, 5 hours.

differences in the height of the dark-colored area (due to slight differences in concentrations of copper oxide and gum arabic) becoming greatly magnified as time proceeds, Series 1, Nos. e, f, g. In order to accept this explanation of the form of the deposits, it is, however, necessary to make the additional assumption that the dark-colored deposit is more readily adsorbed by itself than by the copper crystals,¹ this adsorption taking place upon the upper edge of the dark-colored deposit already laid down. The rising current of electrolyte then accounts for the striae as suggested above.

The striae developed when a higher concentration of copper sulfate (1 M) is employed are more striking than those shown in Series 1. It should also be recalled that these, i.e. the Series 2 photographs, were made at a higher temperature than the Series 1 set.

Rosa, Vinal and McDaniel² have called attention to the fact that increasing the concentration of the electrolyte makes electrolytic striae coarser and more distinct. A comparison of our Series 1 and 2 photographs shows this very clearly. In the case of our Series 2 photographs it is evident, as would be expected, that with the increased concentration of electrolyte, the areas at which cupric oxide and gum arabic are present in sufficient concentration to produce the dark-colored material are more widely separated. Further examination of the photographs shows that the striae result from these initial areas. Thus, in the fifteen minute deposit of Series 2, small circular areas³ first become visible. The striae grow vertically from these initial areas, finally giving rise to the very distinct striae of Series 2, No. h. Eventually the striae grow together to give a deposit more or less homogeneous in appearance. Further electrolysis (Series 2, No. l) does not change the form of the deposit. Evidently when the surface has reached this condition, deposition (at a higher negative potential) of both copper and adsorption of copper oxide and gum arabic occurs uniformly over the entire surface.

As we have already pointed out, the addition of gum arabic produces an increase in the cathode polarization. The method pursued for determining

¹ This assumption, we feel, is justified from the form of the striae in the Series 2 deposits, for example No. g of this series. The rounded bottom of these striae is always thicker than the upper part, indicating the small amount of dark-colored product formed below the striae is adsorbed upon coming in contact with the material already laid down. As the adsorbable material formed is slight, the upper part of the striae can only grow by the formation of new material. This can only take place until deposition of copper above the dark area begins again.

² Loc. cit.

³ The circular form of this initially deposited dark-colored material and the drop-like form which the bottom of these areas assumes as the areas grow, indicate very clearly that interfacial forces are at work. Free adsorption (i.e. spontaneous adsorption) of the dark-colored substance would lead to a reduction of the interfacial tension at the boundary, copper-solution. As we feel that free adsorption has been proved (Taft and Bingham: Loc. cit.), these rounding forms can scarcely arise as a result of an increase in the interfacial tension. Rather, they must be due to an increase in the plasticity of the material in the deposit. As we have already shown (Taft and Bingham: Loc. cit., Fig. 5), even small amounts of gum arabic in a copper plating bath produce slipping and displacement of the various crystal surfaces over each other. The large amount of gum arabic and copper oxide present in the solutions from which the Series 2 deposits were obtained would undoubtedly produce a still more plastic substance.

this polarization was that of Haring.¹ The polarization measurements were carried out at a constant temperature of 30°C. Some of our results are tabulated below in Table I and shown graphically in Fig. 2.

TABLE I
Cathode Polarization at 30° of 0.5 M CuSO₄, volts

Current Density Amperes per sq. dm.	Con. of gum arabic, 0	grams per 100 cc. 0.15
0.16	0.022	0.038
0.32	0.029	0.054
0.48	0.036	0.061
0.64	0.041	0.069
0.80	0.047	0.072
0.96	0.058	0.083
1.12	0.071	0.096
1.28	0.085	0.11
1.44	0.096	0.13
1.60	0.11	0.15
2.00	0.15	0.19
2.40	0.18	0.22

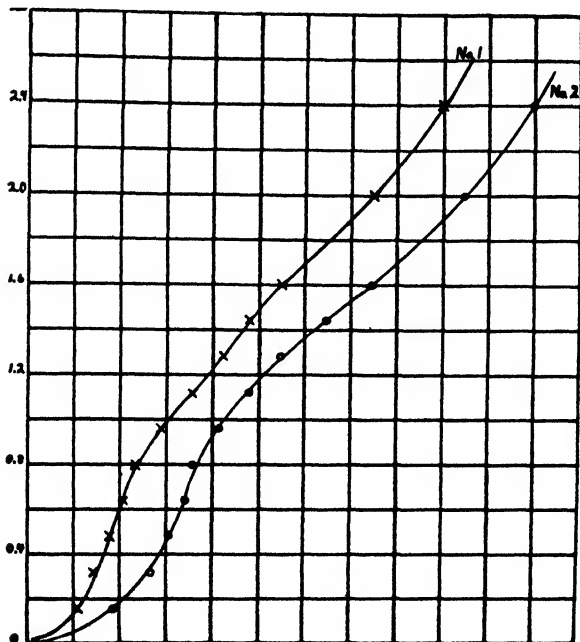


FIG. 2

Abscissae, Cathode Polarization, volts; Ordinates, Current Density, amperes per square decimeter. Curve No. 1 is for 0.5 M CuSO₄; No. 2 for 0.5 M CuSO₄ + 0.15 grams of gum arabic per 100 cc. of solution.

¹ Trans. Am. Electrochem. Soc., 49, 417 (1926).

Similar measurements carried out at lower concentrations of gum arabic gave polarization values intermediate between those given, indicating that polarization becomes greater, at a given current density, the greater the concentration of gum arabic. Incidentally, if the polarization values of Table I are compared with those obtained during the deposition of copper in the presence of gelatin by Taft and Messmore a marked difference is observable. The polarization curves of Fig. 2 duplicate each other in form quite closely. On the other hand, in the presence of gelatin a very marked increase in polarization occurs at a current density of 0.8 amperes. They interpreted this increase to be due to the formation of complex cations between gelatin and copper. Its absence in the present case could be presented as an argument against the existence of any such complex cations of gum arabic and copper.

Summary

1. A photographic record of the growth of electrolytic striations of copper produced in the presence of gum arabic is presented. The formation and growth of these striae can be explained by assuming adsorption of a gum arabic-copper hydroxide complex upon the surfaces of the electrodeposited crystals of copper.
2. The cathode polarization of copper is increased by the presence of gum arabic.

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SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS

Part III. The System Sodium Oleate, Sodium Chloride, Water, Ethyl Acetate

BY E. LESTER SMITH

In the first paper of this series, it was shown that soap solutions have a powerful solvent action for organic liquids of all types. A few observations were also made on the phase equilibria involved on salting out soap solutions in the presence of organic liquids.

It was obviously desirable to investigate in the fullest possible detail one particular quaternary system comprising a pure soap, a salt of the same base, water, and an organic liquid; some of the generalisations made in the earlier paper were in fact based on a knowledge of the behaviour of the system selected. After some preliminary work, it was decided to study the system sodium oleate, sodium chloride, water, and ethyl acetate at 25°. Sodium oleate was chosen because it is more soluble than most sodium soaps and also because it was believed that at 25° it would yield only the two phases, isotropic solution or gel, and curd, and that the anisotropic phases, middle soap and neat soap, would appear only at higher temperatures. This assumption was in fact fallacious and the equilibria proved to be much more complicated than was originally expected. Sodium chloride was chosen as the most generally used salting out agent in previous studies of soap systems. Ethyl acetate had two advantages over most available solvents; when the work was started it was one of the very few organic liquids known which was not permanently emulsified by soap solutions; also being an ester, it could readily be estimated in solutions by saponification with excess of standard alkali and back-titration with acid.

The ready hydrolysability of ethyl acetate, while facilitating its estimation, also introduced an element of risk, namely that the hydrolysis alkalinity of the soap solutions might be sufficient to cause decomposition of the ester during the time necessary for the attainment of equilibrium in the systems. McBain and others¹ have shown that the hydrolysis alkalinity of soap solutions is commonly of the order of $N/1000$, while the concentration of ethyl acetate in sodium oleate solutions may reach $3N$. Calculations from the known velocity constant² indicated that very considerable decomposition of ester and consequently of soap should occur in less than an hour. Fortunately however, ethyl acetate throws back the hydrolysis of soap in the same way as alcohol does. The addition of neutral ester to an aqueous sodium oleate solution, deeply coloured with phenolphthalein, discharges the colour in-

¹ McBain and Martin: *J. Chem. Soc.*, 105, 957 (1914); McBain and Bolam: 113, 825 (1918); Beedle and Bolam: *J. Chem. Ind.*, 40, 27T (1921); McBain and Hoy: *J. Chem. Soc.*, 1929, 589.

² Smith: *J. Chem. Soc.*, 1927, 170.

stantly. The pH of the solution cannot then be much above pH 8, corresponding to an alkali concentration of little more than $N/1,000,000$. This should not be enough to cause appreciable decomposition of ethyl acetate within a day. In practice, slight decomposition can only be detected by the appearance of an abnormal amount of free fatty acid in the ester layer in equilibrium with the soap solution. Such irregularities were not encountered except in the case of solutions which had stood overnight, and normally analyses were completed within a few hours of preparing the mixtures.

The four possible ternary systems will first be considered in some detail. These are best represented graphically in the manner usual for such systems, namely in equilateral triangles, which can later be fitted together to build the tetrahedron which is necessary to express the composition of phases containing all four components. Thus the four corners of the tetrahedron represent the pure components, the six edges the binary systems, the four faces the ternary systems, and the three-dimensional space within the figure, the quaternary system.

In conformity with McBain's usual practice three of the corners represent respectively: 1 *mol* (304 gm) of sodium oleate, 1 *mol* (58.46 gm) of sodium chloride, and 1 *kilo* of water; the remaining corner was made to represent 1 *kilo* of ethyl acetate, which brings this component into line with the other solvent present (the water) and gives a better-spaced diagram than would the use of the sol instead of the kilo. Again following McBain's practice, concentrations of sodium oleate and sodium chloride are expressed throughout in *weight* normalities, i.e. the mols of substance associated with 1 kilo of water, instead of in 1 litre of solution.

The Ternary System Sodium Oleate, Sodium Chloride, Water

A number of soap, salt, water, systems have been studied in detail by McBain and his colleagues,¹ who have shown that all such systems are variants of a single type. The system under study is no exception to this general rule, but is noteworthy in that it shows to an unprecedented degree certain phenomena of metastable equilibria; these phenomena were noted incidentally by McBain and Langdon² but were of unimportant magnitude in the case of the system sodium palmitate, sodium chloride, water, which they were studying.

From preliminary measurements of the solubility of sodium oleate, it was anticipated that although it was more soluble than sodium palmitate, it would behave at 25° like that soap does below 70°, yielding only the two phases isotropic solution and curd. Indeed if the system is studied exactly according to McBain's technique, this appears to be the case. Almost the whole of the diagram is then occupied by a field representing heterogeneous mixtures of curd and isotropic solution or lye, the field of isotropic solutions

¹ McBain and Burnett: *J. Chem. Soc.*, 121, 1320 (1922); McBain and Langdon: 127, 852 (1925); McBain and Elford: 1926, 421; McBain and Pitter: 1926, 893; McBain and Field: *J. Phys. Chem.*, 30, 1545 (1926); McBain, Lazarus and Pitter: *Z. physik. Chem.*, 147, 87 (1930).

² *Loc. cit.*

being limited to a small area in the neighbourhood of the water apex. The technique in question consists in preparing a large number of sealed glass tubes containing sodium oleate solutions, with and without salt, allowing them to curd out, and then observing the temperatures (T_c) at which the curd just redissolves. By suitable interpolation, it is possible to calculate the composition of solution in equilibrium with the curd at 25° . It happens that all such solutions, except those very poor in soap, are gels; since Laing and McBain¹ have shown that these clear isotropic gels do not constitute a phase distinct from the fluid isotropic solutions, this is of no consequence, except that the contents of the tubes cannot be mixed adequately by agitation and a long time has to be allowed for the attainment of equilibrium.

If however, one endeavours to check the values of T_c so obtained, by observing the temperatures at which curd separates on slowly cooling the tubes, the findings are entirely different. Although ample time may be allowed (up to several weeks), curd does not appear until the temperature is reduced many degrees below that at which the curd redissolved. Frequently however, at an intermediate temperature the solution becomes cloudy from separation of globules of a second liquid phase, which the polarising microscope reveals to be anisotropic, and which from analogy with similar systems is assumed to be neat soap. Provided a tube is not cooled sufficiently for curd to separate, this phenomenon is perfectly reversible, and the temperature (T_i) at which the anisotropic phase just separates or disappears can be determined with precision, even though the isotropic phase is a gel. The emulsion of anisotropic phase in isotropic gel can be kept at a suitable temperature for weeks without change (excepting a slight tendency for the globules to coalesce), although the same tube previously cooled until curd separates, may be kept indefinitely at the same temperature or even slightly above T_i , without the curd dissolving completely, and without the appearance of any anisotropic phase.

It is possible to demonstrate this phenomenon even more dramatically in the following manner: three sealed tubes may be prepared each containing the same solution (e.g. sodium oleate 0.22 N_w ; sodium chloride 0.32 N_w) and after heating until the contents become homogeneous, the first may be left in this condition, the second cooled until it contains an opaque mass of curd, and the third cooled until curdling just commences and then warmed again so that it contains numerous nodules of curd dispersed through a clear gel. These three tubes can then be kept indefinitely at any temperature between T_i and T_c (32° to 36° for the solution suggested) without any apparent change taking place in any of them. If the temperature is reduced to a little below T_i , the first (clear) tube becomes cloudy from separation of neat soap, the second remains opaque with curd, while the third shows nodules of curd dispersed through a cloudy emulsion of neat soap in isotropic gel. The nodules of curd in this third tube show no inclination to increase in size or to redissolve at either temperature in the course of a week or so.

¹ J. Chem. Soc., 117, 1507 (1920).

Only when the temperature is reduced to the value T_d , several degrees below T_i , (25° for the solution suggested) do the curd nodules begin to grow in this tube, and to appear in the first tube, until eventually both tubes become filled with masses of curd like the second tube.

It should be noted that in bulk the neat soap phase is not permanently stable at 25° but separates into curd and isotropic solution, although in the form of small globules it appears to be stable for indefinite periods. This fact may perhaps be related to the relative sizes of these neat soap globules and the curd fibres. In terms of the average diameter of the neat soap globules, the curd fibres appeared to have a length of some 50 times, and a thickness of $1/10$ this value. When an emulsion of neat soap in isotropic solution was allowed to cool and curd out on a microscopic slide, the curd fibres appeared to form in the isotropic solution, shooting between the neat soap globules, which gradually redissolved as the isotropic solution became depleted of soap from deposition of curd.

In case any of these findings should be attributed to the presence of less soluble soaps in the sodium oleate employed, a number of the measurements were repeated using sodium oleate made from highly purified oleic acid prepared by Mr. Skellon by the methods described in his recent paper.¹ The results were qualitatively identical, and differed quantitatively only insofar as the temperatures T_c , T_i , T_d , were slightly slower in the case of the especially pure sodium oleate. The author wishes to express his thanks to Mr. Skellon for the gift of this oleic acid.

In order to express these observations in terms of isotherms, it is necessary to draw on the phase diagram (Fig. 1) *three* lines delimiting the field of isotropic solutions. The smallest field P Q water apex, is the one first described, comprising solutions in which curd dissolves completely on warming to 25° ; the second line C R shows the composition of solutions in equilibrium with neat soap: the third M S indicates the composition of solutions still richer in soap or salt, from which curd just separates at 25° .

Thus the usual isotherm representing the solubility of sodium oleate in salt solutions, is replaced by the area PQSM between the first and third of these lines. Any solution, the composition of which is represented by a point within this area, may be in equilibrium with curd.

In the case of solutions poor in salt the temperature T_c and T_d tended to approach one another more closely, and neat soap either did not appear at all on cooling the tube, or appeared as a metastable phase at a temperature below T_d . Thus if the isotherms were drawn for a temperature somewhat below 20° , the lines CR and MS would cross.

Unless these phenomena can be shown to be cases of suspended transformation, it can only be concluded that the Phase Rule in its usual form is not applicable to this system. The observations are however not entirely new, nor is this suggestion without precedent. McBain and Langdon² observed that in the system sodium palmitate, sodium chloride, water, curd is not

¹ J. Soc. Chem. Ind., 50, 131T (1930).

² J. Chem. Soc., 127, 852 (1925).

deposited until the temperature is reduced about 4° below the temperature T_c at which it dissolved, and that often neat soap appears first as a meta-stable phase. Previously Laing and McBain¹ had shown that sodium oleate solutions (without salt) could be obtained at suitable temperatures in the three forms of isotropic solution, isotropic gel, and curd, and further that the concentration of the solution admixed with the curd altered slowly with time, as evidenced by the changing conductivity of the system. These authors explained the phenomena by postulating that the solubility and degree

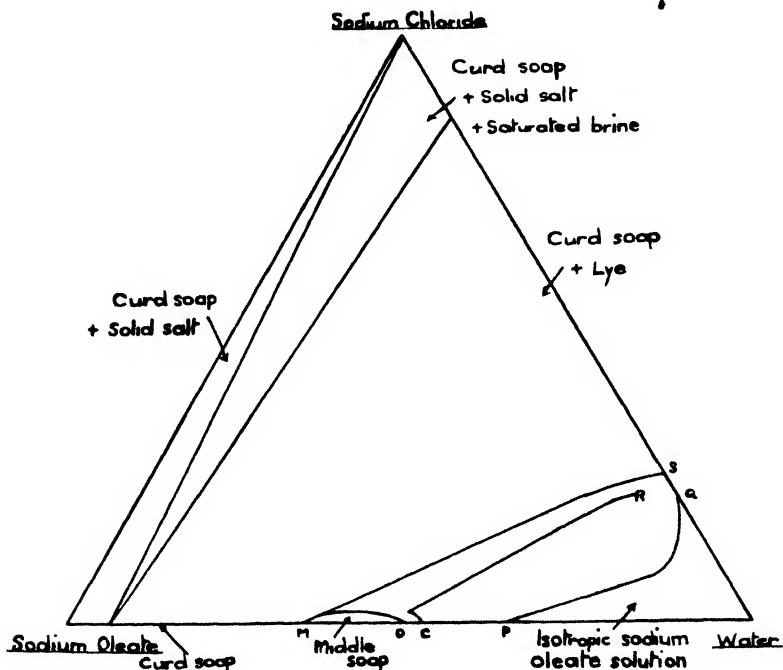


FIG. 1

of hydration of the curd fibres is a function of their diameter, in the same way that the solubility of a crystalline solid is greater when it is very finely divided. In other words they suggest that for these systems the Phase Rule takes the form of $P + F = C + 3$, the extra degree of freedom being the diameter of the curd fibres. They nevertheless express the opinion that given sufficient time at a fixed temperature, a soap curd, soap solution, system will reach a definite equilibrium. This is tantamount to saying that the extra degree of freedom is merely a temporary property of the system and that only one diameter of curd fibre (presumably the largest possible), is permanently stable. The present study not only provides more striking illustrations of the necessity for revision of the Phase Rule in connection with soap curd systems, but also calls into question the temporary nature of the extra degree of freedom; the observations recorded above can all be explained

¹ J. Chem. Soc., 117, 1507 (1920).

by assuming that the fine curd fibrils have a considerable greater solubility than the coarse fibres. Thus consider a solution which has been allowed to curd out at a low temperature; the curd will be in the form of coarse fibres, and on slowly warming, the last curd fibre will evidently dissolve at the temperature (T_c) at which a solution of this composition is just saturated with respect to the coarse fibres. On cooling again, curd can only be deposited in the form of fine fibrils which subsequently grow; but the solution is not saturated with respect to these fibrils until the temperature is reduced considerably below T_c . Moreover, before this lower temperature is reached the solution may, if the concentrations of sodium oleate and sodium chloride are within certain limits, become saturated with respect to neat soap; since supersaturation with a liquid (or liquid crystal) phase cannot occur, even in soap systems, neat soap promptly separates out at the temperature T_i . At a still lower temperature, for which the symbol T_d is used, the solution becomes saturated with respect to the fine curd fibrils. Once these are deposited they can grow and extend without further reduction of temperature, because the solution is already supersaturated with respect to the coarse fibres. Yet the supersaturation which exists between the temperatures T and T_d cannot be regarded in the same light as an ordinary suspended crystallisation i.e., as a metastable condition, because if the solution could be seeded with fine curd fibrils, these would not grow but would dissolve, since the solution is not saturated with respect to the fine fibrils. Even if the solution is seeded with the coarse fibres, further deposition of curd does not occur, because this is still dependent on the prior formation of fine fibrils. This fact is illustrated by the third tube in the experiments described above, in which a solution remained permanently in equilibrium with particles of curd over a range of temperature. A sodium oleate system containing curd may probably reach a final equilibrium state *provided the temperature is below T_d* , but between T_c and T_d the state of the system depends on its previous history, and a condition of "arrested equilibrium" holds indefinitely. Experimentally the temperature T_d is difficult to ascertain with precision, because supersaturation readily occurs with respect to the fine curd fibrils. Moreover, since a solution in the neighborhood of the temperature T_d is usually cloudy with separated neat soap globules, the soap concentration of the isotropic solution which remains is of necessity lower than that of the solution as a whole, so that the temperature T_d at which curd is deposited really represents the temperature at which some solution differing in composition by a small unknown amount from that of the bulk, is in equilibrium with fine curd fibrils.

Neat soap may justly be regarded as a metastable phase at 25° despite its stability in the emulsified state since if the globules could be made to coalesce the mass of neat soap would undoubtedly deposit curd. It is possible that the appearance of neat soap may be taken as the equivalent of the separation of curd, but even so it seems impossible to explain the discrepancy between T_c and T_i except by postulating an extra degree of freedom in the system, namely the dependence on fibre diameter of the solubility of soap curd.

Middle Soap

Having established the existence of neat soap as a metastable phase at 25° , it was natural to look for the second anisotropic phase, middle soap, which McBain has found to be common to a number of soaps. It was found that no sodium oleate solution which has curded out will yield middle soap on warming to 25° . Middle soap is stable at higher temperatures however, and some of these solutions remained unchanged on cooling to 25° ; when the soap concentration was above a certain limit however, they gradually curded out at 25° . The precise limits of this region on the phase diagram were not determined.

Hydration of Curd

No method is available to determine the hydration of curd when the lye with which it is in equilibrium is a gel, which was the case in this system except when the salt concentration was so high as almost completely to salt out the soap.

The System Sodium Oleate, Water, Ethyl Acetate

The only systems of this type which have previously been investigated in any detail are those in which the organic component is phenol or cresol.¹ The addition of soap progressively increases the mutual solubility of these substances and water, up to the point of complete miscibility; the triangular phase diagrams for these systems therefore show binodal isotherms. These studies are however incomplete, since at higher soap concentrations additional phases such as curd soap would appear, which are not indicated on the published diagrams.

At temperatures above 60° , the system sodium oleate, water, ethyl acetate, behaves in a similar fashion, but at 25° the mutual solubility of ethyl acetate and water is not sufficiently augmented by the soap to render the components completely miscible in any proportions.

The area A B C water apex on the phase diagram (Fig. 2) includes all isotropic sodium oleate solutions containing ethyl acetate. Solutions represented by points on the line A B are saturated with ethyl acetate, and are in equilibrium, as represented by the tie-lines, with ethyl acetate containing traces of water, soap, and fatty acid.

The author has pointed out in a previous publication² that the presence of a solvent layer in equilibrium with the soap solution increases the degree of hydrolysis of the latter, by removing fatty acid and so disturbing the hydrolysis equilibrium.³ In the present study it was essential to ignore this hydrolysis if the number of components was to be limited to four. Fortunately the error so introduced was small.

¹ Bailey: J. Chem. Soc., **123**, 2579 (1923); Weichherz: Kolloid-Z., **49**, 158 (1929); Angelescu and Popescu: **51**, 247 (1930).

² Analyst, **53**, 632 (1928).

³ Holde: Z. Elektrochemie, **16**, 436 (1910); also McBain and Buckingham: J. Chem. Soc., 1927, 2867, and the recent criticism of this work by Wellman and Tartar: J. Phys. Chem., **34**, 379 (1930).

TABLE I
The System Sodium Oleate, Sodium Chloride, Water

Sodium Oleate	Sodium Chloride	Water	T _c	T _i	T _d (approx.)	Remarks
74.0	0	26.0			> 25°	Middle soap, curding at 25°
62.1	0	37.9	> 25°		< 25°	Middle soap at 25°
49.5	0	50.5		> 25°		Middle soap + isotropic at 25°
47.5	0	52.1		25°		
47.1	0	52.9	34°	5°	16-20°	
46.7	0	53.3	32°	—		No anisotropic phase separates on cooling
44.5	0	55.5	27.5°	—	16-20°	" " "
41.5	0	58.5	27°	—	16-19°	" " "
37.5	0	62.5	26.5°	—	19°	" " "
32.5	0	67.5	26°	—	19°	" " "
38.6	6.0	55.4		17°	20°-24°	
38.3	6.6	55.1		22.5°	20°-24°	
37.7	8.1	54.2	30°-32°	27°		
27.5	7.9	64.6		12°	20°-24°	
25.8	6.1	68.1		11°		
25.0	13.0	62.0		22°	20°	
24.5	14.3	61.3		25°		
23.5	15.9	60.6	37°	32.5°	20°-25°	
22.3	5.1	72.6	27°	8°	19°-22°	
21.1	4.1	74.8	21°-25°	—	18°	" " "
19.7	19.4	60.9		32°	25°	
15.3	15.2	69.5	32°-36°	< 25°		
14.5	20.9	64.6	36°	32°	25°	
14.3	6.6	79.1	28°-30°	8°	19°-21°	
*14.3	22.0	63.7	39.5°	31°	25°-27°	
*14.2	22.4	63.4	40°	32.5°		
14.1	18.7	67.2	32°-36°	27°		
13.4	23.4	63.2		42.5°	> 27°	
13.0	22.4	64.6	32°-36°	31°	25°	
*11.2	6.4	82.4	< 25°	—	< 15°	" " "
10.2	17.0	72.8	32°-36°	< 25°		
* 8.1	23.7	68.2	39°			
7.4	21.0	71.6	35°		21°-25°	
5.45	10.2	84.35	28.5°	—	19°	" " "
4.0	14.1	81.9	25.5°	—		" " "
* 3.9	14.8	81.3	27°	—	19°-21°	" " "
3.7	22.6	73.7	40°	36°	20°-25°	
* 2.2	12.2	85.6	21°-24°	—	19°-20°	" " "

* Extra pure sodium oleate.

At the point B, the solution is also saturated with sodium oleate, and a new phase appears. This phase takes the form of a very soft translucent plastic gel, which shows a brilliant play of colours on examination with a polarising microscope. From considerations of its composition and properties, there is no doubt that from the Phase Rule point of view, this liquid crystal phase is correctly designated as neat soap. When it is in equilibrium with isotropic solution and ethyl acetate its composition is necessarily fixed and

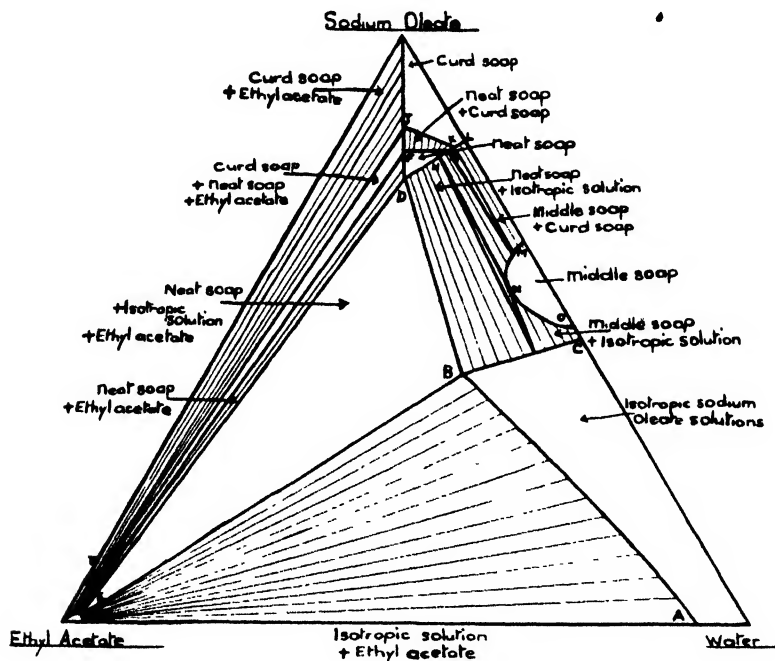


FIG. 2

is represented by the point D on the diagram. Neat soap does not persist as a stable phase at 25° in absence of ethyl acetate, so that the limits for its existence are represented by the area DFG which does not touch the sodium oleate, water, side of the triangle. Along DF, the neat soap is in equilibrium with ethyl acetate, along FG, with curd soap, and along DH, with isotropic sodium oleate solutions. The area FGKJ represents heterogeneous mixtures of neat soap and curd soap, which at F and J are also in equilibrium with ethyl acetate forming an invariant system.

The area MNO represents approximately the limits for the existence of middle soap. This phase can absorb a little ethyl acetate but breaks down to a mixture of neat soap and isotropic solution before the soap becomes saturated with the ester.

Experimental

The position of the line AB on the phase diagram, and of the tie-lines connecting this with the ethyl acetate corner, were determined as follows:

weighed quantities of a sodium oleate solution of known strength, and of ethyl acetate were shaken together in a separating funnel, and allowed to attain equilibrium and separate in a thermostat at 25°. Ethyl acetate was then estimated in both layers by determining the volume of standard alkali required to saponify the ester. A suitable quantity of the lower layer was run into a flask containing 25 ml of N/2 sodium hydroxide. The flask was immediately restoppered and reweighed, then heated slightly and set aside for about 15 minutes, after which the contents were back-titrated with N/2 hydrochloric acid using phenolphthalein as indicator, sufficient neutral ethyl alcohol being added to make the concentration about 50% in the final solution, to prevent hydrolysis of the soap from obscuring the end-point. About 2 gm of the upper layer were weighed into a flask containing 50 ml of sodium hydroxide, and treated similarly. A larger quantity of the upper layer was evaporated to dryness and the residue weighed to determine the sodium oleate present. The water in the upper layer was estimated by difference. The point B was fixed by measuring the quantity of water required just to dissolve the neat soap in a mixture of isotropic solution, neat soap, and ethyl acetate, of known composition.

The areas near the sodium oleate apex were less easy to delimit accurately. The principal reason for this lay in the instability of the ethyl acetate. It was impossible to heat mixtures in sealed tubes in order to render them homogeneous, because the ethyl acetate was rapidly hydrolysed. For the same reason, it was not permissible to allow mixtures to remain at 25° to attain equilibrium, for longer than a few hours. It was therefore necessary to rely on shaking and stirring at the temperature of the observations in order to mix the components. The examination under the polarising microscope of mixtures of known composition prepared in this manner gave some indication of their nature. The position of the line DL was also fixed approximately by an analytical method, similar to that used by McBain and his colleagues to determine the degree of hydration of soap curd.¹ Sodium chloride was used as the reference substance, the assumption being made that it is not sorbed by the neat or curd soap in the presence of ethyl acetate. Although this assumption may not be true, the error introduced is not likely to be very large, and since it is impossible to eliminate the sources of error mentioned above, other reference substances suggested as more suitable by McBain and Martin and by Laing² were not tested.

The further assumption is involved that the degree of hydration of the neat soap is not materially altered by a small concentration of salt in the solution with which it is in equilibrium. A small quantity of sodium chloride solution was added to a soap solution containing less than the saturation concentration of ethyl acetate. After allowing some hours for the attainment of equilibrium, a portion of the isotropic solution was separated from the anisotropic phase (which slowly rose to the top on standing) and analyzed

¹ McBain and Martin: *J. Chem. Soc.*, 119, 1369; Laing: 1669 (1921); Bennett: 125, 1971 (1924).

² *Loc. cit.*

for soap, salt, and ester. The ethyl acetate was estimated by the method described above except that sulphuric acid was used for the titration. Excess acid was then added, the liquid boiled to remove alcohol, and the oleic acid extracted with ether and weighed after evaporation of the ether. The aqueous layer was warmed to remove dissolved ether, neutralised with sodium hydroxide, and titrated with N/10 silver nitrate using potassium chromate as indicator. These analytical data, together with a knowledge of the original composition of the mixture, enable the composition of the neat soap to be calculated. In some cases the mixture of neat soap and isotropic solution which remained was analysed as a check. Further, the concentration of ethyl acetate required to saturate the isotropic solution was known from other experiments, and by making the additional assumption that on satura-

TABLE II
Composition of Phases in Equilibrium

Lower Layer			Upper Layer		
Sodium Oleate	Water	Ethyl Acetate	Sodium Oleate	Water	Ethyl Acetate
—	92.73	7.27	—	2.9	97.1
8.3	82.7	9.0	1.0	2.85	96.15
15.8	73.2	11.0	1.0	2.7	96.3
24.6	61.5	13.9			
27.2	58.3	14.5	1.0	2.7	96.3
32.5	50.4	17.1	1.2	2.8	96.0
38.5	42.8	18.7			
39.8	40.4	19.8			
42.3	37.3	20.4	In equilibrium with ethyl acetate layer and neat soap (point B) (Neat soap in equilibrium with ethyl acetate) (hetero. neat soap + curd soap)		
42.2	37.3	20.5			
77.7	11.3	11.0			
80.3	11.7	8.0	Neat soap in equilibrium with isotropic solution and ethyl acetate (point D)		
74.5	13.5	12			
75.5	12.5	12			
75.5	12.5	12			
76	12	12			
78	11	11			
80.5	9.5	10	Neat soap in equilibrium with curd and ethyl acetate		
80.5	15	4.5	Neat soap in equilibrium with isotropic solution (containing Na Cl)		
79	13	8			
60	36.5	5.5	Homo. middle soap		
58	36	6	Middle soap in equilibrium with isotropic solution		
57	35.5	7.5	Heterogeneous; neat soap + isotropic solution		

tion the ester concentration in the neat soap would increase in the same ratio as in the isotropic solution, it was possible to fix the point D. Fair agreement was obtained between several determinations using different concentrations of ester and salt.

The limits of the middle soap region were determined approximately by dissolving ethyl acetate in sodium oleate solutions of appropriate concentration, and observing the amount which could be added before the mixture became heterogeneous. This was detected by a decrease in viscosity and a change in the appearance of the mixture under the polarising microscope.

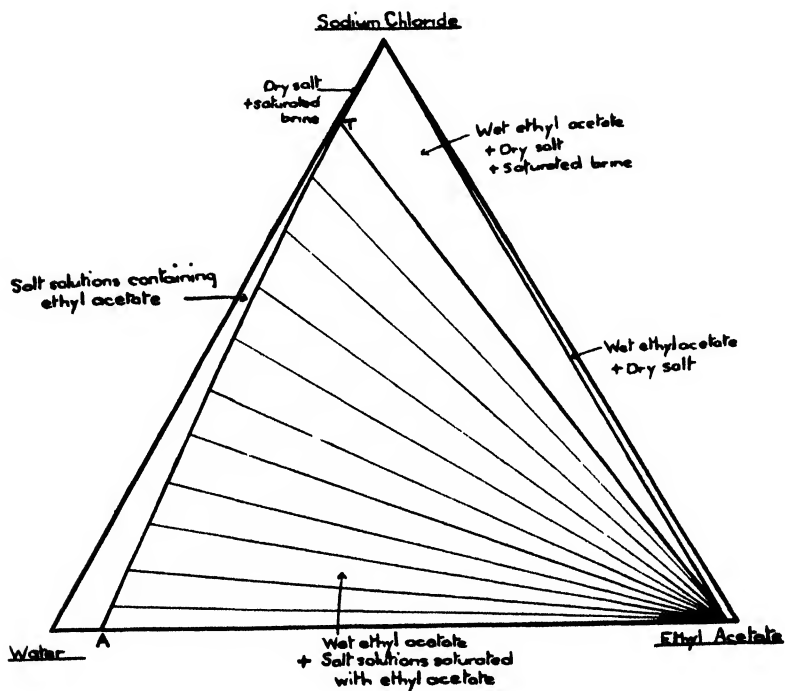


FIG. 3

The System Sodium Oleate, Ethyl Acetate, Sodium Chloride

Sodium oleate and ethyl acetate appear to be almost completely immiscible in the absence of water. The solubility of dry sodium oleate in the dry ester was found to be only 0.005%. It is almost impossible to determine whether the sodium oleate absorbs any of the ester, but the dry powdered soap did not swell or undergo any obvious change even in boiling ethyl acetate. Sodium chloride is completely immiscible with both the other components.

The System Sodium Chloride, Ethyl Acetate, Water

The solubility of ethyl acetate in water is depressed by additions of salt, the ester being "salted out." The solubility of water in ethyl acetate is also slightly decreased by increases in the salt concentration of the aqueous

phase with which it is in equilibrium, owing to the dehydrating effect of the salt. These observations are illustrated by the position of the line AT and the tie-lines in Fig. 3. At T the aqueous phase is saturated with salt, which appears as a third phase. The brine and salt are in equilibrium with ethyl acetate containing 1.6% of water, which value therefore indicates the extent to which the wet ester could be "dried" by contact with sodium chloride. The diagram is completed by two very narrow triangles containing tie-lines linking, in the first case, solid salt with ethyl acetate containing less than 1.6% of water, and in the second case, linking solid salt with brine not saturated with ethyl acetate.

Experimental

Weighed quantities of the three components were shaken together in a 100 cc separating funnel immersed in the thermostat until equilibrium was attained. The lower layer was analysed for ethyl acetate as described earlier, except that N/2 sulphuric acid was used for the back-titration, instead of hydrochloric, and the sodium chloride was then estimated as a check in some cases, by titration with N/10 silver nitrate using potassium chromate as indicator. The upper layer was also analysed for ethyl acetate, the water being estimated by difference.

TABLE III
Composition of Layers in Equilibrium

Lower Layer			Upper Layer		
Ethyl Acetate	Sodium Chloride	Water	Ethyl Acetate	Sodium Chloride	Water
7.27	—	92.73	97.1	—	2.9
5.4	19.2	75.4	97.15	—	2.85
3.9	34.7	61.4	97.4	—	2.6
2.25	52.7	45.05			
0.6	76.0	23.4	98.0	—	2.0
0.15	85.75	14.1	98.4	—	1.6
(In equilibrium with solid NaCl)					
—	86.0	14.0			
(In equilibrium with solid NaCl)					

The Quaternary System

When the number of components is increased to four, the equilibria become difficult to describe in words, or to represent on a plane surface. However, the quaternary system presents no phases which have not already been described, and with the aid of the diagrams it is not difficult to construct a mental picture of the three-dimensional tetrahedral diagram within which the system can best be represented. This reconstruction can be made most easily from Fig. 4 which represents the tetrahedron opened out, so that the sides are bent back into the plane of the base.

A number of attempts were made to plot projections of the quaternary diagram, such as the orthogonal projection onto a triangle used by Schreinemakers, the orthogonal projection onto a square used by the same author, and the improvement on this method described by Philipsborn¹ but without exception they produced diagrams too confused to be readily intelligible. The projection used by Jänecke, in which the tetrahedral diagram is projected onto a face triangle by lines radiating from the opposite vertex, proved more useful, and as much of this projection as is practicable has been incorporated into Fig. 4.

The principal feature of the quaternary diagram is the figure representing the limits of composition of isotropic sodium oleate solutions, i.e. the extension of the region A, B, C, water apex, in the base triangle. A surprisingly large amount of salt can be dissolved in sodium oleate solutions containing ethyl acetate before the soap is salted out. Similarly many mixtures of curd soap and lye are liquefied to isotropic solution by the addition of ethyl acetate. The figure is characterised by a "ridge" rising from the point B in the base to a point in the line AT close to the salt, water, edge of the tetrahedron.

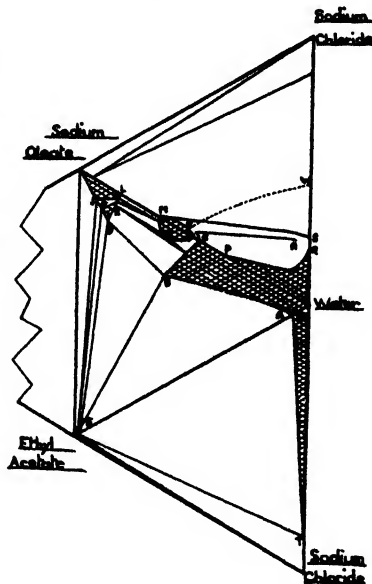


FIG. 4

Projections of this ridge onto both the base triangle and the soap, salt, water, triangle are represented by the lines BU and VW respectively in Fig. 4. One face of the figure, which is almost plane, joins this ridge to the line AB on the base triangle and represents sodium oleate solutions containing salt, in equilibrium with an ethyl acetate layer. A series of tie-lines therefore link this face with points near the ethyl acetate corner. The other face curves away from the ridge, joining it to the line BC on the base and the line CR on the soap, salt, water, face of the tetrahedron. It represents isotropic sodium oleate solutions containing salt and ethyl acetate, in equilibrium with neat soap or curd soap. It is evident that solutions of compositions represented by points along the ridge, must be in equilibrium with both neat soap and ethyl acetate, like the solution represented by the point B on the base triangle. Since, however, the number of components is now four, the presence of three phases in equilibrium does not render the system invariant in composition at the fixed temperature of 25°. The triangle B D E on the base, is therefore multiplied into a series of "tie-triangles" linking together points on the "ridge," points along D F on the neat soap region, and points near the ethyl acetate apex. As one passes up the "ridge" from B, the isotropic solutions

¹ Thonindustrie Z., 53, 45 (1929).

become progressively poorer in soap and richer in salt until when the line AT is reached, the soap is completely salted out. The phase in equilibrium with this lye (in the presence of an ethyl acetate layer) is, however, still neat soap, so that the series of tie-triangles extend further, linking points along AT to points along DF on the neat soap region and points near the ethyl acetate apex. The limit is reached at the point T where the lye becomes saturated with salt, and solid salt appears as a fourth phase. The system would now be invariant at a fixed temperature, but it also happens that at 25° another phase makes its appearance, namely curd soap. Thus the five phases solid salt, saturated lye (point T), neat soap (point F), curd soap (point J), and ethyl acetate containing traces of water and soap, are in equilibrium, in addition of course to a sixth phase, vapour, which is understood to be present throughout.

Such a system can only exist at a fixed temperature; the quintuple point was difficult to determine exactly, but is certainly within a few degrees of 25° . The equilibrium is represented in the tetrahedral diagram by an irregular solid figure, mixtures represented by points within which separate into five phases of compositions represented by its five apices.

It will be evident that each face of this invariant figure which does not already lie in one of the faces of the tetrahedron, must throw off a series of tie-triangles (just as each tie-triangle throws off tie-lines from its edges). The tie triangles linking ethyl acetate, neat soap, and lye or isotropic solution have already been mentioned. Another series link ethyl acetate, solid salt, and curd soap saturated with ethyl acetate, merging finally into the ethyl acetate, salt, soap, face of the tetrahedron. Other tie-triangles link solid salt, saturated brine, and curd soap not saturated with ethyl acetate, merging finally into the salt, brine, curd, triangle in the salt, soap, water, face of the tetrahedron. Still another series link neat soap and curd soap, (not saturated with ethyl acetate) first with a series of salt solutions, then with soap solutions containing salt and a little ethyl acetate.

Experimental

The experimental methods used in the investigation of the quaternary system are for the greater part similar to those described previously. The compositions of isotropic solutions in equilibrium with both ethyl acetate and neat soap were determined in a few cases by gradually adding sodium chloride solution to an isotropic soap solution mixed with excess ethyl acetate, until neat soap just began to separate at 25° ; the isotropic solution was then analysed for salt soap and ester. Subsequently it was found that when an excess of salt was added, the neat soap gradually rose to the surface with the excess ethyl acetate, and a clear sample of the isotropic solution could be withdrawn from the bottom of the vessel for analysis.

TABLE IV
Composition of Phases in Equilibrium

Lower Layer				Upper Layer			
Na OI	H ₂ O	Et \bar{A}	Na Cl	Na OI	H ₂ O	Et \bar{A}	Na Cl
8.1	51.0	6.7	34.2				
8.5	56.7	7.1	27.7	1.5	2.5	96.0	—
22.8	55.5	12.6	9.1	1.9	2.6	95.5	—
32.4	39.7	16.3	11.6				
35.9	40.0	18.1	6.0				
0.8	52.4	3.1	43.7	In equilibrium with ethyl acetate layer and neat soap "Ridge" of figure.			
5.9	50.3	5.2	38.6				
9.9	48.5	7.4	34.2				
11.9	47.5	8.2	32.4				
21.6	42.5	11.7	24.2				
22.9	41.3	11.8	24.0				
30.5	39.5	15.4	14.6				
2.6	59.2	2.9	35.3	In equilibrium with neat soap			
3.2	57.3	3.6	35.9				
4.2	57.0	4.8	34.0				
5.6	62.9	2.5	29.0				
5.8	55.6	2.6	30.0				
7.2	54.0	3.1	35.7				
7.7	58.0	3.3	31.0				
9.2	56.0	4.0	30.8				
9.7	52.4	4.2	33.7				
12.4	53.6	5.4	28.7				
13.8	52.6	6.0	27.6				
16.8	49.8	7.4	26.0				
18.6	53.3	2.8	25.3				

Equilibrium between isotropic solution and neat soap

Isotropic solution				Neat soap		
0.7	50.65	0.95	47.7	80.5	15	4.5
—	37.7	1.2	61.1	79	13	8
—	21.0	0.44	78.6	78	11.1	10.9

Discussion

The phenomena observed in studying the system salt, soap, water, which were incidental to the main purpose of these papers, were discussed in the appropriate section. The system soap, water, ethyl acetate, has also been considered from the Phase Rule aspect, but it is now proposed to examine the findings from the point of view of the colloid chemistry of soap solutions.

The nature of the solvent power of sodium oleate solutions for organic liquids was discussed in part 1 of this series where it was shown that the dissolved liquid may be divided into that dissolved by the aqueous dispersion medium, and that dissolved or adsorbed by the colloidal soap.

The data now available render possible a quantitative treatment of the special case where the organic liquid is ethyl acetate.

A solution of sodium oleate saturated with ethyl acetate will again be treated as a two phase system. It will be assumed as a first approximation that the hydration of the colloidal soap is zero, or rather, that the whole of the water in the solution is free to dissolve the normal proportion of ethyl acetate. The difference between this and the total weight of ethyl acetate dissolved indicates the weight of ethyl acetate associated with the soap in the solution; this figure, divided by the weight of the soap, evidently gives a value for the apparent solubility of the ester in sodium oleate—*apparent*, because actually this portion of the ethyl acetate is carried only by the *colloidal* soap. When this calculation is applied to the data in Tables II and IV the apparent solubility value is found to increase as the soap concentration increases, because a greater proportion of the soap is in the colloidal state in the more concentrated solutions. A value for the true solubility of ethyl acetate in colloidal sodium oleate may be obtained by the following expedient: if the apparent solubility values are plotted against the reciprocals of the square roots of the corresponding soap concentrations, a nearly straight line is obtained, which may be extrapolated to zero $\frac{1}{\sqrt{[\text{sodium oleate}]}}$. This ob-

viously corresponds to a hypothetical infinite soap concentration, and the solubility value so obtained may be taken as that of ethyl acetate in colloidal sodium oleate. This value is 1.57 gm of ethyl acetate per gm of sodium oleate, or 5.4 molecules of ethyl acetate per molecule of sodium oleate. This figure divided into the apparent solubility values, gives some indication of the proportions of soap in the colloidal state at various soap concentrations. The results are shown in Table V.

It is interesting to note the effect of adding salt to a sodium oleate solution in presence of ethyl acetate. The total amount of ester dissolved of the soap solution is scarcely affected; it is slightly decreased at low soap concentrations, and slightly increased at higher concentrations. This is illustrated in Fig. 4; the line BA represents the solubility of ethyl acetate in absence of salt, and the line BV which is the projection of the "ridge," represents the solubility in soap solutions containing the maximum of salt.

It must be recalled, however, that the solubility of ethyl acetate in water is depressed by salt, so that when the total ethyl acetate dissolved by a soap solution is separated into the proportion dissolved by the water and the proportion associated with the soap, it is found in every case that the latter value is increased by additions of salt (see Table V). This is to be attributed to an increase in the proportion of soap in the colloidal state, and may be compared with a similar conclusion expressed in Part II as a result of partition coefficient

measurements. It may further be noted that although these values for the apparent solubility of ethyl acetate in sodium oleate are higher than any observed in the absence of salt, they never quite reach 1.57, which tends to confirm the conclusion that this value obtained by extrapolation represents correctly the solubility of ethyl acetate in colloidal sodium oleate.

TABLE V

TABLE V			Excess Et \bar{A}	
$[\text{Na } \bar{\text{O}}\text{I}]$ in N_w	$\frac{1}{\sqrt{[\text{Na } \bar{\text{O}}\text{I}]}}$	$[\text{Na Cl}]$ in N_w	$\text{Na } \bar{\text{O}}\text{I}$	α
0.100	3.16	—	0.98	.625
0.216	2.15	—	1.09	.695
0.400	1.58	—	1.20	.765
0.467	1.465	—	1.21	.77
0.645	1.245	—	1.28	.82
0.900	1.055	—	1.32	.84
0.988	1.005	—	1.38	.88
1.130 (max)	0.94	—	1.36	.87
	0 (by extrapolation)—		1.57	1.00
0.150	—	0.490	Not saturated Na Cl	.78
0.159	—	0.671		.97
0.411	—	0.164		.80
0.816	—	0.294		.88
0.898	—	0.150		.89
0.015	—	0.835	Saturated with Na Cl	.57
0.117	—	0.770		.86
0.204	—	0.707		.97
0.251	—	0.681		.99
0.555	—	0.580		.85
0.772	—	0.370		.88

Generally speaking, the proportion of soap in the colloidal state, calculated as described above, increases progressively with increase in the salt concentration, but insufficient data are available for mathematical treatment. It should be understood that values calculated by this method can only be approximate in view of the assumptions involved, and that they stand in need of confirmation by methods similar to those which have been applied to soap solutions in the absence of organic liquids.

Similar calculations can fruitfully be applied to the system sodium oleate, water, *o*-cresol, at 20°, studied independently by Bailey¹ and by Angelescu and Popescu.² In this case, the triangular phase diagram shows a complete binodal curve (although Angelescu and Popescu investigated only the water-rich section). The solubility of *o*-cresol in water is less than that of ethyl acetate but high enough to account for an appreciable proportion of the *o*-cresol dissolved by soap solutions. Allowing for this, values for the apparent

¹ J. Chem. Soc., 123, 2579 (1923).

² Kolloid-Z., 51, 247 (1930).

solubility of o-cresol in sodium oleate have been calculated as described above; they increase steadily from 2.0 to 4.1 gm. o-cresol per gm of sodium oleate as the soap concentration increases, showing no tendency to approach a maximum. The reason for this may be that the concentration of soap never becomes very high, the maximum value being less than one third of that attained with ethyl acetate as the third component. A point worthy of attention however is the very high solubility of o-cresol in sodium oleate. At the maximum the value is 4.1 gm. of o-cresol per gm. of sodium oleate, and since a proportion of the soap must be in molecular solution, the true value must be higher. In terms of molecules, each soap molecule is associated on the average with at least 11.5 molecules of o-cresol.

There is no doubt that these solutions have still a colloidal nature, as Angelescu and Popescu have shown by measurements of their viscosities and surface tensions; nor is it possible to regard the cresol as the solvent, for the solutions are in equilibrium with a cresol-rich phase; if therefore the ionic micelle consists as McBain suggests¹ of about ten oleate ions joined together at the hydrocarbon ends of the chains, there seems no escape from the conclusion that each such micelle must be capable of adsorbing over a hundred cresol molecules.

Summary

The four ternary systems and the quaternary system possible with the four components, sodium oleate, sodium chloride, ethyl acetate, and water, at 25°, are described.

The system sodium oleate, sodium chloride, water, is peculiar in that it constitutes an exception to the Phase Rule; an extra degree of freedom is demanded because the solubility of sodium oleate curd fibres is a function of their diameter. Neat soap separates from certain solutions as a metastable phase.

The components sodium oleate, ethyl acetate, and water, yield the six phases:—isotropic sodium oleate solution, middle soap, neat soap, curd soap, wet ethyl acetate, and vapour.

Sodium oleate, sodium chloride, and ethyl acetate are almost completely immiscible.

The mutual solubility of ethyl acetate and water is depressed by additions of sodium chloride up to the point where the salt appears as a third phase.

The quaternary system introduced no new phase; it is noteworthy for an example of an equilibrium between six phases, namely:—neat soap, curd soap, salt, brine, ethyl acetate and vapour.

The nature of the solubility of ethyl acetate in sodium oleate solutions is discussed. It is possible to calculate approximately from the data the proportion of soap in the colloidal state in sodium oleate solutions.

¹ J. Am. Chem. Soc., 30, 1636 (1928).

THE PROBLEM OF LIQUID SODIUM-AMALGAMS

(A case for the colloid view)

BY G. R. PARANJPE AND R. M. JOSHI

In a discussion of colloiddally disperse structures in metallurgy, Freundlich¹ observes: "It has been pointed out on various sides, with justice, that in the metallurgy of alloys the existence only of true solutions of the components in question or of coarsely disperse system has been assumed, but that no good reason can be seen why colloiddally disperse structures should not frequently exist. It is difficult, no doubt, to characterise them, since, as is obvious, almost all our usual methods for proving the existence of the colloidal state fail us." And as an instance of these colloiddally disperse structures in iron-carbon alloys he points out after Benedicks² that troostite is to be regarded as a colloidal solution of cementite in ferrite.

It was thought, therefore, that it would be interesting to study, in this connection, some of the binary systems in alloys. Recently, much work has appeared on sodium-mercury alloys. And since it is easier to apply colloidal considerations to liquid systems than to solid, it was decided to start with liquid sodium-amalgams in the first instance.

Some General Considerations

Bornemann³ had pointed out that only the following methods can be employed to determine the composition of these alloys:

- (i) The investigation of the thermal diagrams,
- (ii) The study of physical properties other than freezing points,
- (iii) The preparation and examination of micrographs.

And consequently all the research on this problem has proceeded along these lines. Vanstone⁴ studied the problem of liquid as well as solid amalgams of sodium by all these methods. Later, some other physical properties came to be studied by different workers and now sufficient data have been obtained so as to permit of some generalization regarding the structure of the system Na-Hg.

Supposing that the system Na-Hg is a colloid system, it is evident that it can vary in its physical properties in the following among other ways:

- (i) total concentration of the disperse phase,
- (ii) shape of the colloid particle,
- (iii) size of the colloid particle,
- (iv) mass of the colloid particle and
- (v) charge on the colloid particle.

¹ "Colloid and Capillary Chemistry," translated by Hatfield, 805 (1922).

² Z. physik. Chem., 52, 6 (1905); Kolloid-Z., 7, 290 (1910).

³ Metallurgie (1919).

⁴ Trans. Faraday Soc., 6, 42 (1911); 9, 291 (1914) and other papers.

Considering even these variables, there is room enough for inconsistencies to creep into the results when we examine the system merely from the concentration-change point of view. Variations may be caused by any one or all of the other variables, for they depend largely on the method of preparation and by other conditions which may not always be the same. So far, all the various physical properties that have been examined have been studied only with the concentration of Na as a variable, and there appear to be many inconsistencies in the data obtained by different authors, especially when the same properties have been studied by different workers in different laboratories. Thus, in the data on electrical conductivities, we have four different versions of what happens after the initial decrease with increasing concentration.¹ Hine² finds that the conductance of sodium-amalgam passes through a minimum; Vanstone³ states that the conductivity-concentration curve exhibits a maximum corresponding with NaHg₂; D. Bohariwalla and others⁴ obtain two discontinuities, one at 0.079% Na and one at 0.272% Na; while Davies and Evans⁵ report only one, viz., at 0.272% Na. Experimental inaccuracies certainly could not affect the results to such an extent. The inconsistencies can, however, be easily understood if the colloid hypothesis is assumed, and it is noted that the methods of preparation of the amalgams of different workers were all different. Hine prepared his amalgams by diluting an electrolytically prepared, highly concentrated amalgam; Vanstone by adding mercury to pure, oxide-free sodium; D. Bohariwalla by stopping the electrolysis in the electrolytic method at different stages, i.e. by concentrating dilute amalgams; and Davies and Evans by adding sodium to pure mercury. Thus, according to this hypothesis the method of preparation of an amalgam is a factor of great importance.

Another and a very curious example of how the method of preparation affects the properties of an amalgam has recently been supplied by Willstätter, Seitz and Bumm⁶ who point out that amalgams of the same concentration of Na, but prepared in different sorts of vessels such as porcelain dish, or an iron vessel, or a hessian crucible have widely different reducing properties and very different rates of reaction with conductivity water. They, however, attribute it to the impurities coming from the walls of the vessels in which the amalgams are prepared. But this behaviour seems to be strikingly similar to that witnessed in the preparation of Kohlschütter silver sols⁷ which differ in their colour and other properties simply because they are prepared in vessels of different glasses. Thus, in order to define an amalgam a mere statement of the concentration of Na does not suffice; the method of preparation at least must be stated.

¹ Cf. Bornemann and Müller: *Metallurgie*, 9, 473, 505 (1912).

² *J. Am. Chem. Soc.*, 39, 879 (1917).

³ *Trans. Faraday Soc.* 9, 291 (1914).

⁴ *Ind. J. Physics*, 4, 147 (1929).

⁵ *Phil. Mag.*, (7) 10, 569 (1930).

⁶ *Ber.*, 61B, 871-886 (1928).

⁷ *Z. Elektrochemie*, 14, 49 (1908).

Shape and Size of the Particles

Regarding the shape and size of the particles nothing can be said for the present, since no method that could be adapted to study this system has yet been developed. The chief difficulty is that this system is entirely opaque to ordinary light.

Number of Particles in the System

Similarly, we know nothing regarding the number of particles in the system, though it will be perfectly legitimate to imagine an amalgam showing different properties with different proportions of particles of different sizes, though the concentration of the disperse phase is the same.

Charge on the Particles

As regards charge, however, some data are available. Lewis, Adams and Lanmann¹ reported that with the passage of an electric current through a liquid Na-amalgam, sodium always gathers round the anode. Le Blanc and Jäcks² confirmed this. But Kremann and co-workers³ went a stage further and showed that while this is true up to a concentration of 2% Na, at higher concentrations, sodium gathers round the cathode. This, again, is strikingly similar to the change of charge phenomena so often encountered in colloid chemistry.

Theories of the Development of Charge

This raises the question as to how this charge is developed. The explanations so far offered tend generally towards the compound or complex formation view. According to this view a definite compound or a complex of the type of Na_xHg_y is first formed and then is ionised to a certain extent. During the passage of an electric current ordinary electrolysis takes place, sodium going towards one electrode and mercury towards the other. But this explanation, which can be valid only for concentrations higher than 2%, is not quite satisfactory in the case of lower concentrations, for it raises the difficulty as to how sodium which is so electropositive wanders towards the anode, and particularly when it is combined with mercury which is much less electro-positive. This difficulty is got over by some chemists by assuming that the ionisation does not take place as Na_x^- and Hg_y^+ but as $(\text{Na}_x\text{Hg}_y)^-$ and $\text{Hg}_{y/2}^+$. This assumption again is very similar to the assumption of the formation of colloid micellae.

Skaupy⁴ has proposed a theory of charge development according to which metals dissolved in mercury are ionised to a considerable extent. His theory, however, cannot directly be applied to the problem in hand without assuming the formation of sodium-mercury complexes as shown by Davies and Evans.⁵ The conclusion of Davies and Evans would be acceptable if their amalgams

¹ J. Am. Chem. Soc., **37**, 2656 (1915).

² Z. Elektrochemie, **35**, 385-416 (1929).

³ Monatshefte, **46**, 515, 529 (1926); **56**, 35-65 (1930).

⁴ Verhandl. dent. physik. Ges., **16**, 156 (1914).

⁵ Loc cit.

were prepared by diluting concentrated amalgams but they prepared each of their amalgams by concentrating a dilute one.

But, probably, unaware of Skaupy's work, Lewis, Adams and Lanmann¹ formulated a theory based on Kraus's explanation of the ionisation of Na in liquid ammonia and explained the initial decrease in conductivity on the conductivity-concentration curves as due to large aggregates of mercury atoms gathering round sodium atoms and thus reducing the average mobility of the electrons that take part in the conduction of electricity. This conception of Lewis and co-workers appears to be very similar to the formation of a solutoidal colloid.²

Further Confirmation of Lewis's Hypothesis

The assumption of Hg atoms aggregating round Na atoms as nuclei seems to be further supported by Ramsay's observations³ on the lowering of vapour pressure of mercury by dissolved sodium. He found that the molecular weight of sodium when dissolved in mercury falls with increasing concentration and suggested that this might be due to the formation of a stable alloy of sodium and mercury which acts as a solvent. His suggestion regarding a stable alloy of sodium and mercury, however, cannot be accepted and it is probable that mercury atoms aggregate round the sodium atoms as nuclei.

Non-electro-cratic Nature of the Amalgams

Again, if even a part of the conductivity was electrolytic, as assumed by the previous workers, there should be an increase in the total conductivity on addition of sodium and not the observed decrease which takes place, at least, up to the first discontinuity. Thus the conductivity of the amalgams does not appear to be electrolytic at least, in the ordinary sense of the term. D. Bohariwalla and others⁴ have confirmed this to some extent. They measured the conductivity of an amalgam by a direct current method as well as by the induction coil method and found that the values obtained by both these methods were exactly the same. Now, since the conductivity is not electrolytic and there is still the migration of Na towards one electrode or other what was called electrolysis appears to be simply the phenomena of cataphoresis, and the high current densities required to secure the migration show that the system Na-Hg is non-electrolytic. This again is in conformity with the solutoidal or lyophilic nature of the system.

Some Indirect Evidence to support the above Conclusion

There is already some more evidence inherent in the results published from this and other laboratories which points to the same conclusion.

Thus, since Bhatnagar and co-workers⁵ found that Na-amalgams are only slightly activated as regards their inter-action with conductivity water

¹ Loc cit.

² Cf. P. P. von Weimarn: *Rev. gén. Colloides*, 7, 153-158 (1929).

³ *J. Chem. Soc.*, 1889, 521.

⁴ Loc. cit.

⁵ *J. Ind. Chem. Soc.*, 1, 263 (1924).

by exposure to ultra-violet light, it would seem that the ultra-violet light does not produce coagulation. Recent work of N. R. Dhar¹ shows that, broadly speaking, the action of light on colloidal solutions consists in flocculating or at least sensitising a lyophobic sol and stabilising a lyophilic sol.

The lowering of surface tension of mercury by the addition of Na observed by F. Schmidt,² and later confirmed by our observations on the electrocapillary curves for N NaNO₃ against Hg, is also relevant. If the system Na-Hg is assumed to be colloidal it cannot be of a lyophobic type for in such systems the surface tension of a sol does not differ much from that of the dispersion medium, but in lyophilic systems there can be a change in the value of the surface tension of the dispersion medium due to the presence of the disperse phase. Thus the observed lowering of the surface-tension of mercury by the addition of sodium indicates that the system Na-Hg is lyophilic or solutoidal.

The increase in viscosity with increase in Na-concentration observed by Bhav³ is strikingly similar to the increase in viscosity with increase in gelatine concentration observed in the preparation of gelatine sols which are extremely lyophilic.

Thus it is seen that the available data obtained from the study of electrical conductivity, surface-tension and viscosity together with the other properties discussed support the conclusion that the system Na-Hg is a *Lyophilic Dispersoid System* with Hg as the *Dispersion Medium*, Na the *Disperse Phase* and (Na_x)Hg_y the Colloid Micellae.

Super-fusion and Super-cooling observed by Vanstone

Vanstone⁴ determined the F. P.'s of a number of amalgams prepared by adding required quantities of mercury to sodium contained in a tube. He started with pure Na and went on to the other end of the scale on his thermal diagram. At all concentrations he observed persistent super-fusion and super-cooling, which indicates that the F.P. of an amalgam is not definite but extends over a small range of temperature. This, according to the colloid hypothesis can be referred to the presence of a number of different micellae of the type (Na_x)Hg_y —with different values for X and Y.

Arrests in Vanstone's Thermal Diagram

Again, Vanstone obtained arrests at the points of discontinuity, the number and lengths of which differed when he attempted a re-determination of a fairly wide portion of his thermal diagram. Having attributed the discontinuities in the thermal diagram to the stages of formation of different compounds or complexes, he explained the arrests as due to the presence of these compounds in polymorphic forms. Now polymorphism is due to the different

¹ "Chemical Action of Light" (1930).

² Ann. Physik, (4) 39, 1108-1132 (1912).

³ Thesis, Bombay University (1927).

⁴ Loc. cit.

patterns in which molecules arrange themselves. In a similar manner the colloid hypothesis attributes the discontinuities to the sudden appearance of new phases i.e. the formation of different types of micellae with different equilibria with the inter-micellar liquid, and the arrests to the different gel-structures that might be formed during solidification, the variations being due to different rates of cooling.¹

Uncertain Composition of the Supposed Compounds

In support of this hypothesis, it may be added, that Vanstone does not claim that the compositions of the compounds he mentions can be stated with any certainty. The indefiniteness of the compounds becomes more apparent from Table I which Vanstone himself prepared, and to which we have added the last column and the last item. It is true that some of the compounds mentioned in it are from the solid regions but the whole emphasizes the point that the compositions of these compounds are uncertain and unreliable. This, on the colloid hypothesis, can be referred to the different proportions of the different micellae, while the compositions assigned by Vanstone appear to be the average of the ratios of sodium to mercury in the several micellae.

TABLE I

Compounds found with their formulae	No. of compounds
NaHg ₅ , NaHg ₆	2 ²
NaHg ₄	1 ³
NaHg ₅ , NaHg ₆	2 ⁴
NaHg ₅ , NaHg ₂ , NaHg, Na ₃ Hg	4 ⁵
NaHg ₅ , NaHg ₆ , NaHg ₂ , NaHg, Na ₃ Hg	5 ⁶
NaHg ₄ , NaHg ₂ , Na ₁₂ Hg ₁₃ , NaHg, Na ₃ Hg ₂	5 ⁷
Na ₃ Hg, Na ₃ Hg ₂ , NaHg, Na ₇ Hg ₈ , NaHg ₂ , NaHg ₄	6 ⁸

The Crystalline Nature exhibited by Vanstone Micrographs

Vanstone's micrographs cannot be cited as an argument against this hypothesis, for the crystalline structures visible therein are not excluded from the broader view of colloids. In some cases it is known that the colloid state is but an intermediate state between molecularly disperse sols and crystalline precipitates. Indeed, with metal-metal sols, especially when they are solidified, flakes with crystalline appearance are to be expected.

¹ Cf. Freundlich: pp. 613-614.

² Berthelot: Ann. Chim. Phys., (5), 18, 442 (1879).

³ Guntz and Féree: Compt. rend., 131, 182 (1900).

⁴ Kerp and Böttger: Z. anorg. Chem., 25, 1 (1901).

⁵ Maey: Z. anorg. Chem., 29, 119 (1899).

⁶ Kurnakow: Z. anorg. Chem., 23, 434 (1900).

⁷ Schuller: Z. anorg. Chem., 40, 385 (1904).

⁸ Vanstone: Trans. Faraday Soc., 6, 42 (1911).

Curves for Other Properties

Similar remarks are applicable to all the curves obtained by several workers for different physical properties where maxima, minima and discontinuities are obtained. At maxima and minima, especially when they are flat, the colloid hypothesis assumes that the micellae-inter-micellar liquid equilibria are stable over fairly wide ranges of concentrations and that at abrupt discontinuities they are rather unstable. These equilibria depend largely on the method of preparation of the different amalgams.

Derivations from the Law of Mixtures observed by T. W. Richards

T. W. Richards¹ measured the E.M.F.'s of many concentration cells of liquid Na-amalgams and found that there were considerable deviations from the simple concentration law which holds for true solutions. But, if the system Na-Hg is colloidal, the deviations are to be expected rather than to be treated merely as experimental errors.

Richards also found that the heats of transfer of Na from one amalgam to another calculated by the Helmholtz equation are unusually large. This is not anomalous if the amalgams are colloidal solutions of sodium in mercury.

Change in Viscosity with Time

There is one other phenomenon that can be explained only by the colloid hypothesis. R. V. Barave² observed that the viscosity of dilute liquid amalgams of Na decreases with time and that mere mechanical agitation is sufficient to restore the initial values. His results correct up to 1% for two different amalgams are as follows:

TABLE II

Time	For amalgam A	For amalgam B
1st day	0.01906	0.02757
2nd day	0.01744	0.02151
3rd day	0.01626	0.01669
After shaking on the third day		
	0.01906	0.02760

Thinking that the lowering of viscosity was due possibly to the separation of sodium from the amalgams, he prepared a large quantity of another amalgam and took only a part of it in his viscometer and measured its viscosity from day to day and found similar changes. If sodium was separating, day to day, from the amalgam the initial viscosity of the stored portion which was kept undisturbed for about four days should have been less than the initial value found for the first portion. Actually the initial viscosity of the second portion was if anything greater than that for the first portion. This means that no sodium had separated and that the regaining of the starting

¹ J. Am. Chem. Soc., **44**, 601 (1922).

² Private communication from this laboratory (1928).

value was due to the mechanical agitation the amalgam suffered during its fall into the viscometer. The results of these experiments were as follows:

TABLE III

Time	For amalgam first used	For stored amalgam
1st day	0.01846	0.01887
2nd day	0.01625	0.01699
3rd day	0.01560	0.01539
	On shaking	
	0.01850	0.01885

These results show clearly that without there being any separation of sodium, the viscosity of an amalgam suffers a decrease with time. Woudstra¹ during his coagulation experiments observed a similar decrease in viscosity with time for his silver sols prepared by Wöhler and Muthmann's method. This according to him was due to the coarsening of the colloid particles before complete coagulation occurred. That with the increase in the size of the particles of a sol the viscosity must fall can be seen from v. Smoluchowski's equation.

This deduction has also been confirmed by Odén² from his experiments on sulphur sols, which were completely lyophilic.

Thus the lowering of viscosity of an amalgam observed by Barave is to be referred to the gradual coarsening of the colloid particles which occurs during the ageing of lyophilic sols, and the regaining of the initial or higher value by mechanical agitation to the restoration of the original or greater degree of dispersity. This means that together with the concentration of sodium and the method of preparation, the age and the previous history of an amalgam must be stated if the knowledge about it is to be complete.

Scum Formation

Finally there remains to discuss the phenomenon of scum-formation which has been observed even when the amalgams are kept in an inert atmosphere, e.g. pure dry nitrogen. Up to the present this has been regarded as due to the formation of oxide films. We have taken pains to ensure the complete absence of oxygen and we find that the scum-formation still continues. In the light of the colloid hypothesis, we think that the phenomenon is to be referred to the adsorption of the colloid micellae into the surface which takes place according to Gibbs' law. When the concentration of the disperse phase in the surface layer reaches the appropriate value, coagulation takes place with the formation of solid incrustations. This adsorption reaches equilibrium more quickly with lyophobic than with lyophilic sols. Further experiments in this direction are in progress in this laboratory.

Thus from all that has been said it may safely be concluded that liquid sodium amalgams are lyophilic or hydrargyrophilic sols of sodium in mercury.

¹ Z. physik. Chem., **63**, 619 (1908).

² "Der kolloide Schwefel," p. 102 et seq.

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Summary

1. The considerations of colloid chemistry are applied to the data available on liquid sodium amalgams and it is attempted to show that, unlike the older theories, the colloid hypothesis explains all those results satisfactorily.

2. In the light of this hypothesis it is concluded, (i) that the liquid sodium amalgams are hydrargyrophilic colloidal solutions of sodium in mercury with $(\text{Na}_x)\text{Hg}_y$ as the colloid micellae, (ii) and that a mere statement of the concentration of an amalgam is not sufficient to define it; the method of preparation, the age and the previous history also must be stated with it.

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March 10, 1932.*

VARIATIONS IN EXTINCTION COEFFICIENTS DURING THE COURSE OF JELLY FORMATION

BY SATYA PRAKASH

In previous publications¹ from these laboratories, the details of the methods of preparation of various inorganic jellies have been given. We have also investigated the changes in viscosity and hydrogen ion concentrations during the process of jelly formation.² In a number of cases, the phenomenon of syneresis has also been studied.³ Quantitative experiments have also been made regarding the thixotropic behaviour of thorium jellies.⁴ The influence of organic substances on the setting of various jellies has also been investigated.⁵ On the basis of these results, the mechanism of the formation of jellies has also been advanced, and the views have been applied to explain the nature of the clotting of blood⁶ and gelatinisation of serum.⁷

In the present communication, I am recording my observations on the variations of extinction coefficients during the gelation of the following substances:

Thorium arsenate	Zirconium hydroxide
Stannic arsenate	Ferric molybdate
Stannic phosphate	Thorium molybdate
Mercuri-sulphosalicylic acid	Aluminium hydroxide
Zirconium molybdate	Ferric hydroxide
Zirconium borate	Chromic hydroxide
Ceric arsenate	

The extinction coefficients were measured by a Nutting's spectrophotometer. The jelly forming mixture was placed in a cell 1 cm. thick. The percentage transmission of light at various stages was calculated from the extinction coefficient data. The results are recorded in the following tables.

Thorium Arsenate Jelly

10 c.c. of thorium nitrate solution, containing 12.035 gm. of the salt in 250 c.c., were mixed with 0.9 c.c. of 18% potassium arsenate solution. The total volume was made up to 12 c.c. by the addition of water. The mixture set to a jelly in the course of 20 minutes. The extinction coefficients were measured in green region (5400 Å).

¹ Prakash and Dhar: J. Indian Chem. Soc., 6, 587 (1929); 7, 367, 591 (1930).

² Prakash and Dhar: J. Indian Chem. Soc., 6, 391 (1929).

³ J. Indian Chem. Soc., 7, 417 (1930).

⁴ Prakash and Biswas: J. Indian Chem. Soc., 8 (1931).

⁵ Z. anorg. Chem., 201 (1931).

⁶ Prakash and Dhar: J. Phys. Chem., 33, 459 (1929); 35, 629 (1931).

⁷ Prakash and Dhar: J. Indian Chem. Soc., 7, 723 (1930).

TABLE I

Time in minutes	Extinction coefficient	% Transmission
0	0.18	66.07
6.5	0.20	63.01
12	0.26	54.95
19	0.33	46.77
Set to a jelly		
30	0.40	39.8
45	0.51	30.88
60	0.65	22.39
75	0.72	19.05
90	0.86	13.8
150	0.90	12.5
22 hours	1.51	3.09

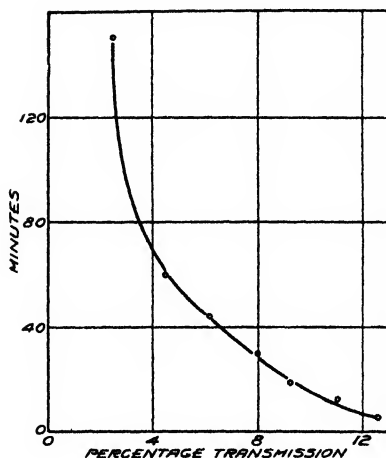


FIG. 1
Thorium Arsenate Jelly (Table I).

When the percentage of transmission of light is plotted against time (Fig. 1), a regular curve is obtained. The curve does not break even at the point of setting. The freshly formed jelly transmits as much as 46% of the incident light but becomes more opalescent on ageing.

Stannic Arsenate Jelly

10 c.c. of M/27.2 stannic chloride solution were mixed with 1.3 c.c. 18% potassium arsenate, and the total volume was made up to 12 c.c. A clear transparent solution was obtained which developed opalescence on standing and finally, set to a jelly in 7 minutes. The extinction coefficients were measured in region 5400 Å.

TABLE II

Time	Extinction coefficient	% transmission
39 sec.	0.07	85.1
2 min. 30 sec.	0.17	67.6
3 min. 30 sec.	0.29	40.6
4 min. 30 sec.	0.56	27.6
5 min. 30 sec.	0.93	11.8
6 min. 15 sec.	1.29	5.13
7 min.	1.73	1.86
Set to a jelly		
8 min.	2.33	0.468
9 min.	2.93	0.118
9 min. 40 sec.	4.00	0.01
10 min.	∞	0

The results show that the opacity increases very rapidly. The jelly is not completely opaque at the time of setting and transmits 1.86% of the incident light, but in the course of the next three minutes, it becomes opaque.

Stannic Phosphate Jelly

To 10 c.c. of M/27.2 stannic chloride were added 2 c.c. of 11% potassium phosphate solution. The mixture set to a jelly in the course of 8 minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE III

Time in minutes	Extinction coefficient	% Transmission
1	0.02	95.5
3	0.08	83.2
5	0.16	69.2
7	0.4	39.8
8	0.72	19.05
Set to a jelly		
9	1.14	7.25
10	2.15	0.56
11	∞	0

At the point of setting, the jelly transmits 19% of the incident light, but it becomes completely opaque on standing for another 3 minutes.

Mercuri-sulphosalicylic Acid Jelly

When 10 c.c. of 1% mercuri-sulphosalicylic acid solution are mixed with 1 c.c. of N/2 potassium sulphate, the mixture sets to a jelly in 50 minutes and the freshly formed jelly transmits as much as 68% of the incident light. The opacity does not rapidly increase with time. However, if the jelly is

prepared by the addition of a larger quantity of potassium sulphate, the jelly is more opaque at the point of setting and develops marked opalescence on standing. 1.0 c.c. of N-potassium sulphate was added to 10 c.c. of 1% mercuri-sulphosalicylic acid. The mixture set to a jelly in 1 minute. The extinction coefficients were measured in the region 5400 Å.

TABLE IV

Time in minutes	Extinction coefficient	% Transmission
15 sec.	0.49	32.4
Set to a jelly		
2 min.	0.56	27.6
6	0.62	24.0
12	0.67	21.4
35	0.75	17.8
60	0.77	17.0

Zirconium Molybdate Jelly

The zirconium molybdate sol was prepared by dialysing a mixture of zirconium nitrate and potassium molybdate for 5 days. Concentration of the sol was 14.48 gm. zirconium molybdate per litre.

To 10 c.c. of the sol, were added 1.2 c.c. of N/20 potassium chloride and the total volume was made up to 15 c.c. by the addition of water. The mixture set to a jelly in 9 minutes. The absorption was observed in the region 5400 Å.

These observations (Table V) show that a slight opalescence is developed when the sol is coagulated by potassium chloride. We have observed that if potassium sulphate were used as a coagulant, there is no appearance of the opalescence in the jelly.¹

TABLE V

Time in minutes	Extinction coefficient	% Transmission
1	0.15	70.8
3	0.15	70.8
5	0.15	70.8
9	0.16	69.2
Set to a jelly		
15	0.16	69.2
33	0.19	64.6
90	0.21	61.7
120	0.21	61.7

Zirconium Borate Jelly

The zirconium borate sol was prepared by dialysing a mixture of zirconium nitrate and borax solutions for four days. Concentration of the sol was 24.72 gm. zirconium borate per litre.

¹ Cf. Prakash and Dhar: J. Indian Chem. Soc., 7, 367 (1930).

10 c.c. of this sol were mixed with 1 c.c. of N-potassium chloride and 1 c.c. of water. The sol set to a jelly in $2\frac{1}{2}$ minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE VI

Time	Extinction coefficient	% Transmission
1 min.	0.04	91.2
1 min. 40 sec.	0.19	64.6
2 min. 30 sec.	0.21	61.7
Set to a jelly		
5 min.	0.21	61.7
7 min.	0.22	60.3
8 min.	0.24	57.5
16 min.	0.27	53.7
30 min.	0.29	51.3

When the sol is coagulated by potassium sulphate instead of potassium chloride, the jelly is quite transparent and does not show marked variations in the extinction coefficients during or after gelation.

Ceric Arsenate Jelly

0.5 c.c. of 18% potassium arsenate solution was mixed with 10 c.c. of 10% ceric ammonium nitrate, containing 30.74 gm. CeO_2 per litre and the total volume was made 11 c.c. by the addition of water. A clear yellow solution was obtained which developed opalescence and finally, set to a jelly in the course of 10 minutes. The extinction coefficients were measured in the region 5400 Å.

TABLE VII

Time in minutes	Extinction coefficient	% Transmission
1	0.20	63.1
2	0.39	40.7
3	0.46	34.7
5	0.74	18.2
8	1.14	7.25
9	1.52	3.02
Set to a jelly		
11	1.82	1.51
13	2.22	0.603
17	2.42	0.380
19	2.62	0.240
21	3.32	0.0479
23	∞	0

It will be seen from these results that the freshly formed jelly transmits about 2.2% of the incident light, but becomes completely opaque in another 13 minutes after setting.

Zirconium Hydroxide Jelly

When sodium acetate is added to zirconium nitrate solution, a clear mixture is obtained which soon develops opalescence and the mixture finally sets to a jelly. To 10 c.c. of zirconium nitrate solution, containing 16.93 gm. of the salt in 250 c.c., were added 1.8 c.c. of 3.84 N sodium acetate and the total volume was made up to 12 c.c. by the addition of water. The mixture set to a jelly in the course of 12 minutes. The absorption was studied in the region 5400 Å.

TABLE VIII

Time in minutes	Extinction coefficient	% Transmission
0.5	0.08	83.2
2.5	0.28	52.5
5.5	0.74	18.2
7.5	1.06	8.71
9.5	1.36	4.36
Set to a jelly		
12.5	1.81	1.55
17	2.56	0.276
23	3.66	0.0219
27	4.0	0.01
30	∞	0

The freshly formed jelly transmits 1.6% of the incident light, but it becomes completely opaque on further standing.

Ferric Molybdate Jelly

To 10 c.c. of 0.929 M ferric chloride were added 5 c.c. of 15% potassium molybdate solution. The mixture was shaken well for 2 minutes, and then filtered. The clean solution set to a jelly in the course of 24 hours. The extinction coefficients were observed in the red region (6500 Å).

TABLE IX

Time in minutes	Extinction coefficient	% Transmission
9	0.82	15.1
35	1.34	4.57
50	1.52	3.02
80	1.82	1.51
110	2.17	0.676
140	2.62	0.240
170	3.02	0.0955
200	3.07	0.0851
260	4.0	0.01
320	∞	0
26 hrs. set to a jelly		

These observations show that much before setting of the jelly, the mixture becomes completely opaque.

Thorium Molybdate Jelly

It has already been shown that the thorium arsenate jelly exhibits marked change in extinction coefficients during and after gelation. Thorium phosphate jellies are perfectly transparent and show only a slight opalescence when preserved for more than 6 months.

Thorium molybdate jelly was prepared by adding 1.4 c.c. of 4.5% potassium molybdate solution to 10 c.c. of thorium nitrate solution containing 12.035 gm. of the salt per 250 c.c. The total volume was made up to 12 c.c. When the solutions were mixed together, the thorium molybdate was thrown down as a white precipitate, which slowly dissolved on shaking. The mixture was shaken for two minutes and the extinction coefficients were taken in the region 5400 Å. The mixture set to a jelly in one hour.

TABLE X

Time in minutes	Extinction coefficient	% Transmission
2.5	0.31	49
4	0.28	52 2
5	0.21	61 7
7	0.18	66 1
11	0.16	69 2
14	0.14	72 5
60	0.14	72 5
Set to a jelly		
90	0.14	72 5
150	0.14	72 5

The fall, in the extinction coefficient in the beginning is due to the fact that thorium molybdate which is thrown down in the form of precipitate is only slowly peptised by the thorium nitrate present in excess. After 12 minutes, there appears to be no change in the extinction coefficients either before or after setting of the jelly.

Aluminium Hydroxide Jelly

The hydroxide jellies were prepared as described in a previous communication.¹ The following solutions were mixed, shaken and filtered:

M/2 aluminium nitrate	4 0 c.c.
3 84 N sodium acetate	2 0 c.c.
2 M ammonium sulphate	2 2 c.c.
4 02 N ammonium	0 8 c.c.

Total volume = 10 c.c. Time of setting = 4½ hours

Extinction coefficients were taken in the region 5400 Å.

¹ Prakash and Dhar: J. Indian Chem. Soc., 7, 591 (1930).

TABLE XI

Time in minutes	Extinction coefficient	% Transmission
7	0.03	93.3
40	0.03	93.3
85	0.035	92.3
135	0.05	89.1
185	0.33	46.8
205	0.45	35.5
222	0.59	25.7
239	0.77	17.0
260	0.90	12.6
275	0.96	10.95
Set to a jelly		
290	1.05	8.91
317	1.09	8.13
335	1.17	6.76
24 hours	1.61	2.46

It will be seen from these observations that the freshly formed jelly transmits about 11% of the incident light, but the opacity continually increases after setting also, but the jelly does not become completely opaque.

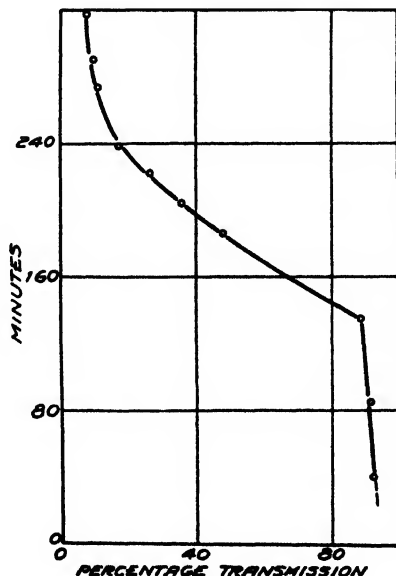


FIG. 2
Aluminum Hydroxide Jelly (Table XI)

When percentage transmission is plotted against time, two definite stages are observed (Fig. 2). For the first 135 minutes, the transparency almost remains constant, but afterwards, a regular steep curve is obtained.

Ferric Hydroxide Jelly

The following solutions were mixed for this jelly:

M/2 ferric chloride	4 c.c.
3.84 N sodium acetate	2.6 c.c.
2 M ammonium sulphate	1.6 c.c.
4.92 N ammonia	0.2 c.c.

Total volume = 10 c.c. Time of setting = 31 hours

Extinction coefficients were studied in the region 6500 Å.

TABLE XII

Time in minutes	Extinction coefficient	% Transmission
4	0.48	33.1
34	0.49	32.4
102	0.51	30.9
224	0.67	21.4
254	0.82	15.1
284	1.12	7.59
314	1.32	4.79
344	1.62	2.40
449	2.12	0.76
525	∞	0
31 hours	Set to a jelly	

The results show that ferric hydroxide jelly becomes completely opaque much before setting.

Chromic Hydroxide Jelly

To 2 c.c. of M/2 chromic chloride solution were added 2.5 c.c. of 3.84 N sodium acetate and 2.5 c.c. of 2 M ammonium sulphate. The mixture was

TABLE XIII

Time	Extinction coefficient	% Transmission
0	0.92	12
4 hours	0.92	12
7 hours	0.92	12
8 hrs. 50 min.	1.40	3.98
10 hr. 15 min.	1.47	3.39
11 hr. 20 min.	1.52	3.02
12 hr.	1.67	2.14
13 hrs.	1.77	1.7
Set to a jelly		
14 hrs.	1.82	1.51
14 hr. 15 min.	1.87	1.35
14 hr. 30 min.	1.92	1.2
24 hr.	∞	0

allowed to stand for one hour, and then, 3.25 c.c. of 4.92 N ammonia were added to it. The total volume was made up to 10 c.c. The mixture set to a jelly in the course of $13\frac{1}{2}$ hours. Extinction coefficients were taken in the region 6500 Å.

From these results, it will be seen that at the point of setting, 1.6% of the light in the region investigated is transmitted, but the jelly becomes completely opaque within 24 hours. When higher concentrations of chromic chloride are taken, the jelly becomes opaque even before setting.

Discussion

The results recorded in the foregoing tables show that the jellies of ferric molybdate and ferric hydroxide become perfectly opaque before their setting, but the jellies of stannic arsenate, stannic phosphate, thorium arsenate, mercuri-sulphosalicylic acid (prepared by coagulating its sol) ceric arsenate, zirconium hydroxide (prepared by mixing zirconium nitrate and sodium acetate), aluminium hydroxide and chromic hydroxide transmit a portion of light when freshly prepared, but the amount of transmission gradually diminishes, as the jellies are allowed to stand for some time. Some of the jellies like stannic arsenate, stannic phosphate, zirconium hydroxide, chromic hydroxide and ceric arsenate become completely opaque sometime after their setting.

The jellies of ferric arsenate, chromium arsenate, ferric phosphate, thorium phosphate, ferric borate, zirconium borate, zirconium molybdate, vanadium pentoxide, and manganese and zinc arsenates do not show any change in extinction coefficients either before or after gelation and they are perfectly transparent.

From these observations, it will be seen that the jellies can be divided into three groups according to their transparency:

(a) Perfectly transparent jellies, which retain their transparency for a long time, e.g., vanadium pentoxide, arsenates of zinc, manganese and iron, thorium phosphate, zirconium molybdate, borate etc.

(b) Jellies opalescent at the point of setting and transmitting only a portion of light, but the opacity increasing with time, and finally, in some cases, becoming perfectly opaque, e.g., the jellies of thorium arsenate, stannic arsenate, phosphate, molybdate, tungstate etc.

(c) Clear sols developing opalescence, and finally, before or at the point of setting, becoming completely opaque, e.g., the jellies of ferric hydroxide, molybdate and tungstate, stannic hydroxide etc.

Very few sols have so far been studied spectrophotometrically, Zsigmondy,¹ Garnett,² Mie,³ Westgren and Reinstötter⁴ and Mukherji and Papaconstantinou⁵ have studied the colour changes of gold sols during coagulation

¹ Ann., **301**, 406 (1898).

² Phil. Trans., (A) **203**, 285, 402 (1904); **205**, 237 (1906).

³ Ann. Physik, **25** (iv), 377 (1908).

⁴ Z. Physik. Chem., **91**, 750 (1918).

⁵ J. Chem. Soc., **117**, 1563 (1920).

and accounted them to the variations in the dimensions of the particles. Miss Roy (now Mrs. S. Dhar)¹ has studied the changes in extinction coefficients of stannic, aluminium, and thorium hydroxides and has observed that the sols exposed to light show a higher extinction coefficient than unexposed sols.

I am of the opinion that the increase in the extinction coefficients is due to the growth of particles. So long as the particles are not much larger in comparison to the wavelength of light, that is, they are in the amicronic or sub-micronic state, they do not place an obstacle in the path of light. But with the continued growth of particles, the optical discontinuity of the medium is manifested as opalescence or turbidity.

When transparent sols are coagulated by means of electrolytes, the charge on the particles is neutralised by the adsorption of the oppositely charged ions and in the view of Smoluchowski,² they tend to agglomerate together through capillary forces or forces of cohesion. As more and more of the particles adhere together, more of the opalescence appears.

From our study of jelly formation, we are led to think, that during the course of jelly formation the uncharged particles develop two tendencies side by side,—the one of agglomeration and the other of hydration. The tendency of hydration begins with the surface hydration and finally merges into the structural hydration. Similar forces of cohesion or the capillary forces which bring about the conglomeration of particles, also cause the adsorption of the solvent medium.

The agglomeration tendency of the particles causes the development of opalescence, while the hydration tendency preserves the transparency of the medium. It appears that the formation of a layer of solvent around the uncharged particles of the sol does not change the extinction coefficients.

In those jellies, where the hydration tendency is much predominant over the agglomeration tendency, no change in the extinction coefficient is expected either before or after gelation. These jellies are quite transparent at the moment of formation and can be preserved as such for a very long time.

When both the tendencies act together, the medium develops opalescence and the depth of opalescence depends upon the extent of predominance of agglomeration tendency over the hydration. So long as the two are in balance, the jellies formed are translucent, and the translucency is maintained for a long time.

In cases, where the agglomeration tendency is stronger than the hydration, and the latter is also exhibited to a marked extent, the changes in extinction coefficients with time are rapid and ultimately the opaque jellies are obtained.

In those sols, where the hydration tendency is negligible in comparison to agglomeration, the particles continually develop opalescence, and the sol may become perfectly opaque also, but it does not give a jelly, and in the end the uncharged particles conglomerate and settle down as a precipitate. These are the hydrophobic sols which exhibit the least change in viscosity during coagulation and are incapable of yielding jellies.

¹ J. Indian Chem. Soc., 6, 431 (1929).

² Z. physik. Chem., 92, 129 (1917).

The two tendencies of the particles much depend upon their specific nature, the nature of the peptiser used, as well as upon the purity of the sol, that is, upon the electrolytes present in the sol in free condition. Thus, under suitable conditions, a hydrophobic sol of high purity and with a favourable peptiser may behave as hydrophilic, and the impure hydrophilic sols behave more or less as hydrophobic, they give rise to opaque jellies or sometimes amorphous precipitates too. It has been observed that the greater the purity of the sol, the more it is capable of developing hydration. Thus, with less pure sols, the jellies obtained are opalescent, while with those sols which have been dialysed for a sufficient time, transparent jellies are obtained. The electrolytes present in the impure sols help in the agglomeration of particles. This fact has been observed in the case of ferric arsenate, ferric phosphate, chromic arsenate and other jellies which are obtained by dialysis.

In the case of zirconium molybdate and zirconium borate jellies, I have observed that more transparent jellies are obtained when coagulation is affected by potassium sulphate than with potassium chloride. From this it appears that a sol may be sufficiently pure for the coagulation affected by bi-valent ions and still it may behave as a less pure sol towards the coagulation with monovalent ions. Gore and Dhar¹ have observed that comparatively impure sols give opalescent coagulum, and this is why the zirconium borate and molybdate sols yield opalescent jellies with chloride ions. However these sols behave as sufficiently pure towards sulphate ions and jellies obtained by these ions are transparent.

It has been observed in many jellies that the transparency goes on decreasing even after the setting of jellies, and no discontinuity in the graph is observed at the point of setting. This fact appears to be in contradiction to the orientation hypothesis of jelly formation, where it is presumed that a jelly is formed by an orderly grouping of the jelly forming units. It seems that jelly formation is a continuous process which begins with the gradual neutralisation of the charge on jelly forming particles with the development of the corresponding amount of hydration, so much so, that the whole of the solvent is superficially or structurally adsorbed by the particles, and is subsequently accompanied by the ageing phenomenon.

On our agglomeration-hydration hypothesis, where a jelly has been supposed to be the limiting case of highly hydrated and viscous mass, the affinity for solvent is gradually diminished as the ageing proceeds, and the tendency to agglomerate is increased. The most transparent jellies as of thorium phosphate, zirconium molybdate, ferric arsenate, etc., also develop slight opalescence when kept for about ten months. In those cases, where the agglomeration tendency is very marked, the opalescence rapidly increases after setting, and the jelly may become completely opaque a few minutes after the setting of the jelly.

It has also been observed in the case of inorganic jellies that the transparency of a jelly can easily be modified by slight alteration of conditions. A sol when coagulated with smaller quantities of electrolytes may give

¹ J. Indian Chem. Soc., 6, 641 (1929).

perfectly transparent jellies, but when coagulated with slightly higher concentrations, will give opalescent jellies. A jelly may be transparent when coagulated by one sort of ions, but be opalescent when coagulated by other ions. Similarly, a jelly may be transparent when freshly formed, but may become opaque on ageing. In view of these facts, I am of the opinion that even such opaque bodies as blood clot and curds should also be regarded as specific cases of jellies along with the transparent jellies of soaps, gelatin, vanadium pentoxide and arsenates of zinc and manganese. In these opaque jellies the agglomeration tendency has given them the opacity and hydration tendency of the particles the structure of a jelly, and so long as the hydration is there, they cannot be separated from the class of jellies.

Summary

1. The variations in extinction coefficients during the process of jelly formation of the following substances have been investigated and the percentage of light transmitted at different intervals has been calculated: ferric, chromic, aluminium and zirconium hydroxides; thorium, stannic and ceric arsenates; stannic phosphate, thorium, ferric, and zirconium molybdates, zirconium borate and mercuri-sulpho-salicylic acid.

2. The results on extinction coefficient show that the jellies can be divided into three classes according to their transparency: (i) perfectly transparent jellies showing no variation in extinction coefficients during the course of gelation or after the setting of the jelly, (ii) the jellies opalescent at the point of setting but opacity increasing with time, and finally, in some cases, becoming completely opaque, (iii) the jellies obtained from clear sols, but becoming opaque before or at the point of setting.

3. The transparency and opacity of the jellies have been explained on the basis of hydration and agglomeration tendencies of the jelly forming particles. The hydration tendency gives rise to transparency and the growth of particles due to the agglomeration tendency gives opacity. Where the two tendencies are balanced, the translucent jellies are obtained.

4. Where the opacity increases even after the setting of the jelly, it has been observed, that the extinction coefficients vary continuously and there is no marked break in the curve at the point of setting. From this it has been concluded that the process of gelation, setting of the jelly and the subsequent ageing are all continuous.

5. With the sols of zirconium molybdate and borate, it has been shown that when they are coagulated by chloride ions the jellies are opalescent, but when by sulphate ions, the jellies are transparent.

6. The impure sols yield comparatively opaque jellies, because in that case, the agglomeration tendency of the particles is more favoured. The greater the purity of the sol, the greater will be the hydration tendency of the particles.

7. Even very transparent jellies develop slight opalescence on long standing due to the growth of particles, and decrease in the free surface and hydration.

8. It has been stated that the differentiation between jellies, gels, clots or curds on the basis of their transparency is not adequate because one and the same jelly may become opaque or transparent according to the slight alteration of conditions.

In conclusion, the author wishes to express his indebtedness to Prof. N. R. Dhar for his very kind interest and guidance in the work.

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THE EFFECT OF APPLIED VOLTAGE ON ELECTROLYSIS IN THE RESIDUAL CURRENT RANGE*

BY GLENN H. DAMON

The problem of residual currents was first thoroughly investigated by Helmholtz.¹ He concluded from his work that the maintenance of a residual current by applied voltages below the e.m.f. of decomposition of the electrolyte is due to the depolarizing effect of dissolved gases. These gases may be originally present in the solution, or they may be dissolved from the electrodes after electrolysis has begun. Either process readily accounts for a continuous current with no visible liberation of decomposition products.

Other investigators² have studied this problem with similar results. Diffusion was found to be one of the principal governing factors, while air dissolved in the electrolyte is of varying importance.

Bigelow³ made a general investigation of residual currents, but some of his conclusions are based on very meagre data. Bigelow believed that the dissolved gases as well as the ions of the electrolyte were capable of conducting the electric current.

All of the investigators mentioned above carried out their experimental work under very similar conditions. The earliest investigators merely used a Daniell cell as the potential source, while the later investigators used approximately the same voltage. As a Daniell cell gives 1.08 volts, it is well below the e.m.f. of decomposition of H_2SO_4 , the usual electrolyte used. Bigelow³ reports experiments in which he varied the voltage from 0.500 volts to 1.696 volts; but as will be shown later in this paper, the procedure employed would not insure that the cell was in equilibrium at each voltage reported. This procedure tends to invalidate the results obtained.

The investigation reported in this paper was undertaken primarily with the object of determining the effect of applied voltage on the residual current. Several other variable factors which might affect the magnitude of the results were also investigated.

Experimental Procedure

The apparatus used in this investigation is shown in Fig. 1. The container (A) was a vacuum desiccator. A Cenco Hyvac pump was used, and it was found possible to evacuate the desiccator to the vapor pressure of the acid electrolyte used. The smooth platinum electrodes (B) had an area of 5.52 square centimeters each, and the distance between them was 1.8 cm. Whenever possible, electrical connections were made through mercury to eliminate

* Contribution from the Chemical Laboratory of Michigan College of Mining and Technology, Houghton, Mich.

¹ Helmholtz: *Pogg. Ann.*, **150**, 483 (1873).

² Nernst and Merriam: *Z. physik. Chem.*, **53**, 253 (1905); Cottrell: **42**, 385 (1903).

³ Bigelow: *J. Phys. Chem.*, **6**, 603 (1902); **7**, 327 (1903).

contact resistance. Mercury switches⁴ were generally used in place of knife-edge switches to insure reproducible contacts. The impressed voltage was determined to within 0.001 volts by means of a potentiometer. A six-volt storage battery was used as the source of potential. A Leeds and Northrup type P galvanometer was used as a micro ammeter. In the last part of the investigation, a more sensitive type R galvanometer was used. As the results on the two instruments checked satisfactorily, no attempt will be made to differentiate between the results obtained by the two instruments. As employed in this investigation the type P galvanometer was sensitive to 0.009 micro amperes. The type R galvanometer was sensitive to 0.000347 micro

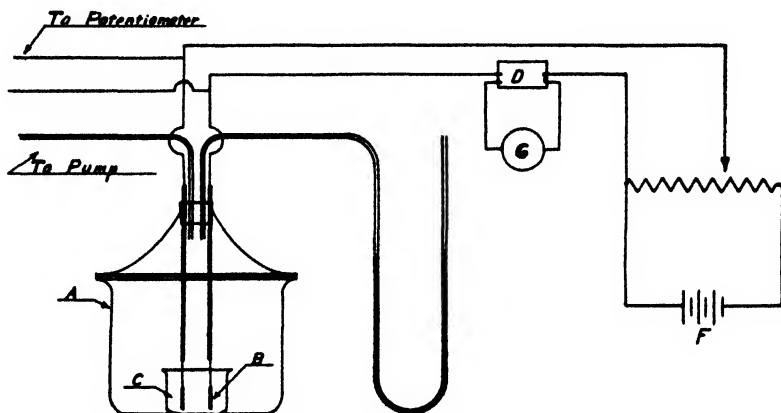


FIG. 1

amperes. By use of a shunt box (D), it was possible to read currents from 0.009 micro amperes up to 7200 micro amperes. All deflections of the galvanometer were read with a telescope.

In the case of all experiments performed in a vacuum, the electrolyte (C) was first boiled and then rapidly cooled before placing in the desiccator. Unless otherwise noted, the apparatus was evacuated for 30 minutes before the switch to the battery was closed; all times given are from the closing of the switch. One-tenth normal H_2SO_4 was used as the electrolyte in all experiments except where the effect of concentration was to be studied. The electrodes were thoroughly washed with distilled water and then heated to incandescence before each run. This last procedure was employed to completely depolarize⁵ the electrodes.

Experimental Results

Most of the work reported in this paper was carried out under reduced pressure. The effect of voltage could have been studied at atmospheric pressure, but it was found possible to get much more consistent results in vacuum than in the air. The results in vacuum are believed to be more satisfactory as this procedure almost completely eliminates the variable factor of dissolved at-

⁴ Damon: *J. Phys. Chem.*, **34**, 2627 (1930).

⁵ Langmuir: *J. Am. Chem. Soc.*, **40**, 1361 (1918).

mospheric oxygen. The difference between the residual current in air and in vacuum is shown in Fig. 2, plotted from the data of Table I. Curve 1 shows the results in air and Curve 2 shows the results in vacuum. A constant impressed e.m.f. of 0.200 volts was used in these experiments. Almost identical

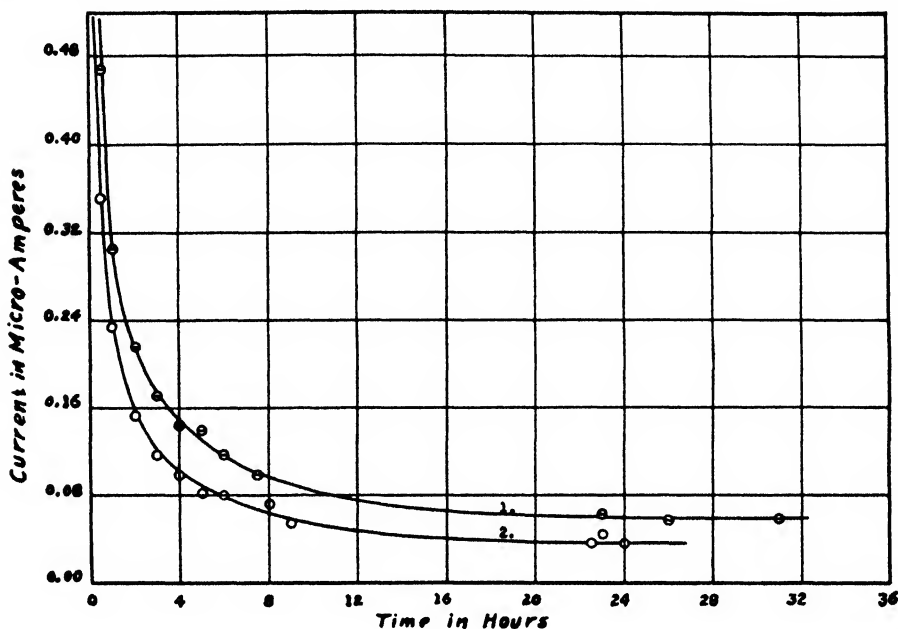


FIG. 2
Relation between Residual Current in Air and in Vacuum

TABLE I
Relation between Residual Current in Air and in Vacuum

Time	I (micro-amperes) in vacuum	I (micro-amperes) in air
$\frac{1}{2}$ hr	0.331	0.468
1	0.234	0.306
2	0.153	0.216
4	0.099	0.144
6	0.081	0.117
$7\frac{1}{2}$	—	0.099
8	0.072	—
$22\frac{1}{2}$	0.036	—
23	0.045	0.063
24	0.036	—
26	—	0.054
31	—	0.054

relationships were found to hold for all work performed at voltages less than 0.75 volts. For higher voltages, the residual current in the presence of air was too variable to make an accurate comparison. This factor is shown more fully in Table III.

The shape of the curves in Fig. 2 are almost identical with those given by Foerster,⁶ Bigelow,³ Helmholtz¹ and others.² However, the absolute value of the residual currents shown in Fig. 2 are of an entirely different order of magnitude than those reported by the above investigators. Where they report minimum currents of several micro amperes, Fig. 2 shows a minimum current of 0.036 micro amperes. This enormous difference can not be accounted for merely on the basis of differences in experimental procedure. However, the reason for this difference becomes apparent when we study the effect of applied potential on the residual current.

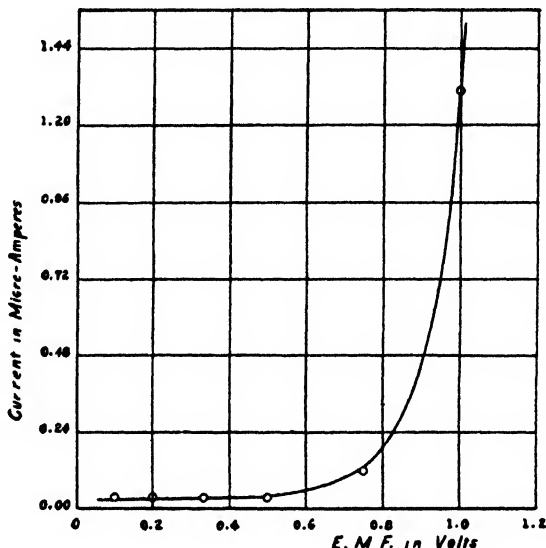


FIG. 3
Relation between E.M.F. and Residual Current

Other investigators^{1,2,3} have impressed one volt or more across the electrodes of their cells. Although this voltage is well below the e.m.f. of decomposition of the electrolyte, it does not necessarily follow that the residual current is independent of the voltage. No experiments are reported by the above-mentioned investigators to show the effect of a greatly decreased potential on the residual current.

TABLE II
Effect of Voltage on the Residual Current

E (Volts)	No. of Runs	Ave. I (micro-amperes)	E (Volts)	No. of Runs	Ave. I (micro-amperes)
0.100	1	0.036	0.500	1	0.036
0.200	2	0.036	0.750	2	0.132
0.335	6	0.036	1.000	2	1.300

Table II and Fig. 3 show (in a summarized form) the effect of different voltages on the residual current. The electrolyte was 0.1 normal H_2SO_4 .

⁶ Foerster: "Elektrochemie," 3rd Ed.

All conditions other than voltage were maintained constant as described under procedure. Each point on the curve represents the average value of the residual current at the end of 24 hours. The individual values which go to make up the average values shown were obtained by runs such as reported in Table I. These data were then plotted as shown in Fig. 2 and the value of the residual current at the end of 24 hours was determined from the graph. This procedure successfully eliminated the effect of any fluctuations which might occur at the time of reading.

The reason for running each experiment 24 hours is evident from a study of Fig. 2. During the first 10 or 12 hours, the current is decreasing very rapidly. However, at the end of 24 hours the current has become practically constant. This constant value for the residual current represents an approximate, if not a true equilibrium value. An attempt was made to obtain a curve similar to that in Fig. 3 by substituting short runs of from one to two hours for the 24 hour runs, but the results so obtained would not check for successive determinations. A fresh sample of H_2SO_4 , taken from the same stock solution, was used in each determination.

The curve in Fig. 3 has two very noticeable features: (1) the almost constant value of the residual current for voltages lower than 0.75 volts; (2) the enormous increase in the residual current for voltages above 0.75 volts.

It is evident that a fundamental change takes place in the phenomena of residual currents between 0.5 volts and 1.0 volts. This conclusion is also confirmed later in Table III and Fig. 4. Evidently the difference in the magnitude of the currents reported in this paper and those reported by early investigators is due to the voltage. Fig. 3 shows that below 0.5 volts the residual current is practically independent of the applied potential. Above 0.5 volts the current is a function of the applied potential. This would seem to definitely disprove the assumption that any voltage well below the e.m.f. of decomposition could be used in residual current work.

No direct reason can be assigned for the break in the potential-residual current curve. Certainly below 0.5 volts we are dealing only with the problem of residual currents. For the higher potentials, there appear to be other effects superimposed on the residual current phenomena. These superimposed effects are apparently a function of the applied potential. An analogy between these effects and actual electrolysis would suggest a secondary decomposition point for H_2SO_4 . This point is apparently very close to one volt, although there is no absolutely sharp break in the curve.

The change in the residual current with voltage might be ascribed as due to the lowering of the decomposition pressure with a decrease in pressure on the electrolyte. Wulff⁷ found that the primary decomposition point of H_2SO_4 was not affected by the varying of the pressure from 0.01 atmospheres to 1000 atmospheres. Knobel⁸ and also Bircher and Harkins⁹ found that the over-voltage is slightly increased by a decrease in the pressure. Since the vapor

⁷ Wulff: *Z. physik. Chem.*, **48**, 87 (1904).

⁸ *J. Am. Chem. Soc.*, **46**, 2751 (1924).

⁹ *J. Am. Chem. Soc.*, **45**, 2890 (1923).

pressure of the electrolyte used in the experiments reported was always more than 0.01 atmospheres, it is evident that the explanation can not be based on decomposition potentials.

As stated before, more satisfactory results were obtained by working in vacuum than in air. In order to compare this work with that of other workers, a comparison was made between the results in vacuum and in air for several different voltages. In Fig. 4, Curve I shows the change in residual current

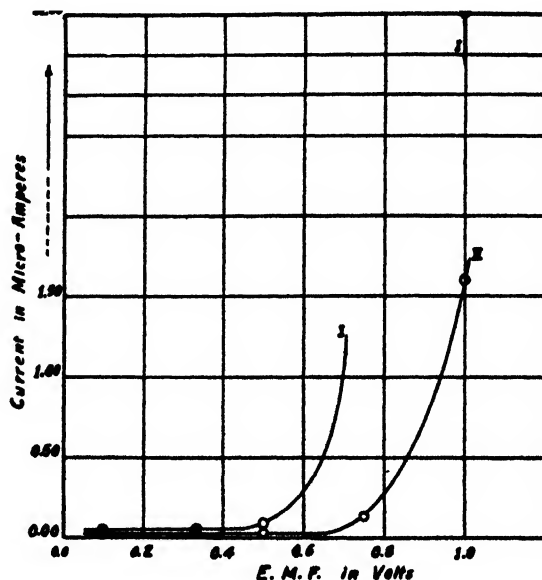


FIG. 4

with voltage when the electrolyte is exposed to the atmosphere. Curve II is the same as Fig. 3 except that it is plotted on a different scale. The ratio of the residual current in air to the residual current in vacuum is shown in

TABLE III

Time in hours	$E = 0.100$	$E = 0.200$	$E = 0.335$	$E = 0.500$	$E = 1.000$
4	2.20	1.44	1.28	3.30	4.13
8	2.10	1.52	1.25	4.08	12.6
12	1.73	1.59	1.30	4.10	14.1
16	1.61	1.60	1.33	3.57	18.0
20	1.56	1.62	1.46	3.00	24.7
24	1.50	1.61	1.66	2.67	33.0
Average	1.78	1.56	1.38	3.45	17.7

Table III. The results shown indicate that air has a greater effect on the residual current for high voltages than for low voltages. The data shown verify the earlier statement that the results are more consistent at low poten-

tials than at high potentials. The data for the higher voltage scarcely warrant the calculation of an average value, but the ratio at the lower voltages is quite uniform.

Fig. 3 and Fig. 4 certainly lead to the conclusion that there is a fundamental difference in the phenomena at high and at low voltages. It is probable that at the higher voltages there is a decomposition effect superimposed on the true residual current.

The experimental work presented in this paper does not disprove the generally accepted theory of residual currents, but it does show that quantitative data on residual currents can not be obtained with potentials much above 0.50 volts. Quantitative data of previous investigators have included at least one factor other than residual current.

The author wishes to acknowledge his appreciation of the helpful suggestions given by Dr. O. P. Watts, Department of Chemical Engineering, University of Wisconsin, at whose suggestion this work was originally started.

Summary

1. Data are presented to show that the magnitude of the impressed e.m.f. has a marked effect on the magnitude of the residual current.
2. Above 0.5 volts, it is shown that the residual current is a function of the applied potential, while for low voltages the residual current is practically independent of the potential.
3. The relationship between the residual current in air and in vacuum is shown for five different potentials.

INDUCED AND PHOTOCHEMICAL OXIDATIONS AND THEIR IMPORTANCE IN BIOLOGICAL PHENOMENA

BY C. C. PALIT

We have been carrying on for the last 8 or 9 years some work on slow and induced oxidation and have studied their importance in biological phenomenon. In a series of publications¹ from this laboratory, we have emphasised the wide applicability of induced reactions and numerous reducing agents have been used as inductors. Ferrous and cerous salts and sodium sulphite are inductors which have been largely investigated. Numerous organic compounds and food materials have been oxidised simply by passing air at the ordinary temperature through solutions or suspensions of the substances in contact with freshly precipitated ferrous hydroxide or cerous hydroxide which acts as an inductor. Similar results have been obtained with sodium sulphite as inductor. We have induced the oxidation of substances like carbohydrates, fats and nitrogenous substances etc. by air at the ordinary temperature by mixing the above substances with sodium sulphite, ferrous hydroxide, cerous hydroxide and other reducing agents. The slow oxidation of these reducing agents set up the oxidation of carbohydrates, fats and proteins. We have been able to establish that induced oxidations are of general occurrence and that the mechanism of the oxidation can very well be explained.

In order to explain the mechanism² of these induced oxidations in the presence of ferrous and cerous salts, the formation of higher oxides like FeO_2 (Manchot³) and Ce_2O_5 (Job⁴) has been assumed; and these higher oxides oxidise the difficultly oxidisable substances like the food materials. Our experimental results⁵ on the oxidation of sodium formate by air in presence of ferrous and cerous hydroxides lend support to the hypothesis of the intermediate formation of the higher oxides.

From our experimental results⁶ on the induced oxidation of glucose by air in presence of ferrous and cerous hydroxides it will be seen that the induction factor—i.e. the ratio of the amount of oxygen taken up by glucose to the amount of oxygen taken up by inductor is as high as 8 or 9. Similar results are also obtained with other reactions. Spoehr also obtained a value as high as 15 for the induction factor. It therefore, appears that the oxidised form of the inductor viz. Fe_2O_5 or CeO_2 etc. is also capable of oxidising the acceptor, thereby regenerating the original inductor. Hence these induced reactions

¹ Z. anorg. allgem. Chem., **122**, 146 (1922); **144**, 289 (1925); J. Phys. Chem., **28**, 943 (1924); **29**, 376, 799 (1925); **30**, 939 (1926); **32**, 1663 (1928); **36**, 711 (1930).

² J. Phys. Chem., **35**, 2043 (1931).

³ Ann., **314**, 177 (1899); **325**, 93 (1902); **460**, 179 (1927).

⁴ Job: Ann. Chim. Phys., (7) **20**, 207 (1900).

⁵ Palit and Dhar: J. Phys. Chem., **34**, 711 (1930).

⁶ Palit and Dhar: J. Phys. Chem., **29**, 799 (1925); **30**, 937 (1926).

appear to be partly catalytic in nature but inasmuch as the rate at which the original inductor is regenerated is small as compared with the rate of its oxidation, these reactions belong more to the induced type rather than the catalytic one.

These higher values of the induction factors can be satisfactorily explained from the point of view of the generation of ions in the primary exothermal reaction. Thus for example, a small amount of an inductor is oxidised; some ions will be generated in this exothermal reaction and the ions will activate some molecules of the acceptor or the actor or both. These then will react. This reaction being exothermal will in its turn give rise to more ions which will activate some more molecules of the reactants and so on. Thus the oxidation of a small quantity of the inductor brings about the oxidation of a large amount of the acceptor, that is, the slow oxidation of the reducing agents (inductors) set up the oxidation of carbohydrates, fats, proteins and other food materials.

It is well known that the edible substances like carbohydrates, fats and proteins are very readily oxidised in the body, whereas they are oxidised with difficulty by ordinary laboratory reagents. We have carried on our experiments¹ and have been successfully able to induce in the laboratory the oxidation of edible substances like glucose, starch, milk, butter, egg-white, egg-yellow and also the oxidation of other substances like cholesterol, lecithin, glycerol, etc. at the ordinary temperature by passing a slow stream of air in presence of inductors like sodium sulphite, ferrous hydroxide, cerous hydroxide, etc.

It has also been shown² that not only fats but carbohydrates and nitrogenous substances are oxidised by hydrogen peroxide and a ferric salt at 37°, volatile aldehydic or ketonic compounds being formed. We³ have conclusively proved in a systematic manner that fats, carbohydrates and nitrogenous and other organic substances can be completely oxidised into their main end products, carbon dioxide and water by air with the help of an inductor ferrous or cerous hydroxide or in presence of sunlight at the ordinary temperatures and we have thus been able to imitate successfully the physiological process of oxidation on which animal life depends. It appears, therefore, that the intermediate iron peroxide obtained in the case of hydrogen peroxide and ferric or ferrous salts must be different from that formed with ferrous compounds and oxygen, because the products of oxidation are different in the two cases.

We have also carried on investigations⁴ on photochemical oxidation of each of substances investigated in connection with the slow and induced oxidations. It is interesting to note that all these substances—such as glucose, lactose, maltose, starch, glycogen, glycine, urea, glycerol, hippuric, and uric acids, formate, tartrate, stearate, oleate, etc. and complex edible sub-

¹ J. Phys. Chem., **34**, 711 (1930).

² J. Ind. Chem. Soc., **6**, 617 (1929).

³ J. Phys. Chem., **34**, 711 (1930).

⁴ Palit and Dhar: J. Phys. Chem., **32**, 1263 (1928); **33**, 1897 (1929); **34**, 737 (1930); **34**, 993 (1930); Z. anorg. allgem. Chem., **191**, 150 (1930).

stances such as butter, milk, egg-white, egg-yellow, carbohydrates, etc. can be readily oxidised by passing air through them if they are exposed to sunlight without catalyst or inductor. In each of these cases, complete oxidation to carbon dioxide takes place. Even the most complex substances like butter, milk, egg-white, egg-yellow, lecithin, cholesterol, glycerol, etc. are oxidised quantitatively into carbon dioxide and water.

Our results on induced and photo-chemical oxidation of all the substances investigated conclusively prove the following facts:

Induced Oxidations

1. The oxidation of fats is retarded by carbohydrates or less powerfully by proteins and to a greater extent by a mixture of carbohydrates and proteins.
2. The oxidation of proteins is markedly retarded by carbohydrates and fats.
3. When fats are rapidly oxidised due to the absence of the negative catalyst, glucose, acetone bodies are likely to be generated in the body. Apparently the easily oxidisable carbohydrates which act as negative catalyst in the oxidation of fats are necessary for the complete combustion of fatty food materials; the oxidation of both fats and carbohydrates can go on slowly and simultaneously.

The view that diabetes is due to insufficient oxidation of glucose and fats in the animal body, has been emphasised by us in one of our previous publications.¹ In other words, the disease is caused by want of catalysts or enzymes which in normal health exist in the body and help the oxidation of glucose, fats, etc. It seems pretty certain that disappearance of acetone bodies from diabetic urine due to the injections of insulin is an effect caused by the increased oxidation of glucose in the body. We suggested in one of our publications that insulin extracts of yeast, vitamins, etc. activate the catalysts or the enzymes and consequently act as accelerators in the oxidation of glucose by air in the system. It may be that minute traces of iron or sulphur are present in insulin, extract of yeast, vitamins, etc. and that this iron present in a very reactive state, is the active substance which helps the oxidation of glucose by air. As from our researches, we find that iron is a very important catalytic agent in many oxidation reactions and that iron in some form or other is essential for life and plays an important part in the oxidation reactions in plants and animals. Hence we urge on medical people to treat diabetes by the internal use of iron salts or colloidal iron preparations which will act as an accelerator in the oxidation of glucose and fats by oxygen.

In one of our publications² from this laboratory it was suggested that insulin and other allied substances are good reducing agents and are readily oxidised by atmospheric oxygen and the oxidation of these substances induces the oxidation of sugar in the body. We have now been able to substantiate this view by our new sets of oxidation experiments on insulin and glucose.

¹ Palit and Dhar: *J. Phys. Chem.*, **32**, 1663 (1928); **31**, 1259 (1927).

² *J. Phys. Chem.*, **29**, 376 (1925).

For these experiments a definite volume of air freed for carbon dioxide was passed through an aqueous solution of insulin (B.D.H.) kept at 25° and the amount of carbon dioxide obtained by oxidation of insulin was absorbed by standard barium hydroxide solution and estimated as usual. When glucose is added to the insulin solution and the same volume of air is passed through the mixture, glucose is slowly oxidised and this can be shown by estimation of glucose by Fehling's solution, which, however, cannot be reduced by insulin. In this experiment with insulin and glucose, the oxidation of insulin which is readily oxidised by air at ordinary temperature leads to the oxidation of glucose thus corroborating our previous statements.

In several publications,¹ we have emphasised the importance of induced oxidations in understanding the phenomenon of animal metabolism. It has been stated that the readily oxidisable substances like glutathione and other substances present in muscle and in other parts of the body, are first oxidised by the inhaled oxygen and these oxidations induced the oxidation of food materials. Insulin and other internal secretions also appear to be readily oxidised in the body and these lead to the oxidation of carbohydrates, fats and proteins. It is now well-known that in the treatment of acute diabetes, repeated doses of insulin have to be injected in order to get satisfactory results. Our experiments on the oxidation of insulin by air show that it is used up by the oxidation in the body and thus repeated doses are necessary. Moreover the oxidation of insulin leads to the oxidation of glucose in the body and this explains the decrease of glucose in the diabetic blood and urine on injection of insulin.

(5) Animal life is assumed to depend essentially on the catalytic activity of the enzymes and iron in the animal body. It is likely that in the animal body, there exist readily oxidisable substances such as enzymes containing traces of iron in complex colloidal condition and the oxidation of these substances induce the oxidation of food materials.

(6) In the animal body, the iron in the blood accelerates catalytically the oxidation of food stuff by the peroxide formed in the body from the inhaled oxygen. When there is a deficiency of iron in the blood, the animal becomes anaemic. At this stage any iron salt preferably of colloidal nature taken in the body, will supply the natural deficiency and the necessary amount of oxidation will take place.

(7). We also suggest that fever is an auto-catalytic reaction. The oxidation of substances like starch, sugar, proteins, fats, etc. by oxygen in the animal body is believed to be catalytically accelerated by the parasites or secretions of bacteria. Hence the amount of heat generated in the animal body for unit time is increased and the phenomenon of fever is observed. Moreover like all other chemical changes, the amount of oxidation in the animal body for unit time is also increased by the incipient rise of temperature.

¹ J. Phys. Chem., 35, 2043 (1931).

(8). From our quantitative experiments¹ on the oxidation of carbohydrates, glycerol, fats and proteins by air in presence of freshly precipitated ferrous and cerous hydroxides and sodium sulphate as inductors, we have shown that the amount of carbon dioxide obtained in these slow oxidations is practically the same as is expected from the point of view that the carbohydrates, glycerol, fats and nitrogenous substances are completely oxidised into carbon dioxide and water by passing air at the ordinary temperature. Similarly Spoehr has obtained considerable amounts of carbon dioxide from the induced oxidation of carbohydrate by air in presence of sodium ferrous and ferric pyro-phosphates. We are of opinion that these results are of importance because these oxidations are of the same type as those taking place in the animal body. Hence we emphasise that in normal health, the food materials taken in the body are completely oxidised into carbon dioxide and water without the formation of intermediate compounds, just as food materials are completely oxidised to carbon dioxide and water when air is passed through their solutions or suspensions in presence of inductors. Intermediate compounds are only formed in the diseased condition of the animal body.

(9) Voit stated "that the metabolism in the body was not proportional to the combustibility of the substances outside the body, but that protein which burns with difficulty outside metabolises with the greatest ease, then carbohydrates, while fat which readily burns outside is the most difficultly combustible in the body." This conclusion was arrived at by Voit from actual feeding experiments on animals. We have obtained quantitative and comparative results² on the velocity of oxidation of fats, proteins and carbohydrates by air and thus tried to establish whether fats or carbohydrates are oxidised more readily in the system. Our results show that the order in which they are oxidised in presence of cerous hydroxide are as follows: egg white > egg-yellow > starch > glucose > butter. In presence of cerous hydroxide, the induced oxidation of fats, nitrogenous substances and carbohydrates follows the same order as stated by Voit.

(11) The experimental results³ show that carbohydrates, proteins, fats and other substances are oxidised in presence of inductors in neutral and alkaline solutions, and the greater the amount of alkali, the greater is the amount of oxidation. Hence we are of opinion that alkaline treatment should prove efficacious in gout, diabetes, beri-beri, rickets and other metabolism diseases, because in presence of even sodium bicarbonate, the amount of oxidation of fats, carbohydrates and nitrogenous substances is greatly increased.

Hence all these results on slow and induced oxidation of fats, nitrogenous substances and carbohydrates occurring either singly or in mixtures by air at ordinary temperature are important, because these oxidations are of the same type as those taking place in the animal body.

¹ Palit and Dhar: *J. Phys. Chem.*, **34**, 711 (1930); and *Z. anorg. allgem. Chem.*, **191**, 150 (1930).

² Palit and Dhar: *J. Phys. Chem.*, **34**, 711 (1930).

³ Palit and Dhar: *J. Phys. Chem.*, **29**, 799 (1925); **30**, 939 (1926).

Photochemical Oxidation and Physiological Experiments

(1) Aqueous solutions or suspensions of the following substances have been oxidised by passing air in presence of sunlight:¹ arabinose, cane sugar, galactose, glucose, lactose, laevulose, maltose, starch, glycogen, urea, glycine, α -alanine, hippuric acid, sodium urate, potassium oxalate, sodium formate, sodium tartrate, potassium stearate, potassium oleate, potassium palmitate, lecithin, glycerol, cholesterol, butter, egg-white, egg-yellow and milk. Zinc oxide, uranium nitrate and ferric nitrate act each as a photosensitiser in the oxidation of the above substances and the amount of oxidation of these substances is greater than that in their absence.

(1) Our results² also show that the amount of oxidation increases with (i) the intensity of light, (ii) the amount of light falling in the solutions and (iii) the time of exposure.

(2) Dilute solutions of lactic acid, oxalic acid, tartaric acid and citric acid are appreciably oxidised by air in presence of sunlight and the order in which they are oxidised is: oxalic > lactic > tartaric > citric.

(3) In order to find out whether in presence of sunlight the carbohydrates, fats, and nitrogenous substances are oxidised completely to carbon dioxide or other intermediate products are formed, we have estimated the amount of carbon dioxide obtained in these oxidations in potash bulbs. The amount of oxidation of these substances was also, in all cases, estimated by direct analysis. The experimental results³ show that the amount of oxidation determined from carbon dioxide obtained is practically the same as the oxidation found out from the direct analysis of the carbohydrates, fats and nitrogenous substances remaining unoxidised. Hence in presence of sunlight, different carbohydrates, fats and nitrogenous substances can be completely oxidised by air at the ordinary temperature into their main end products, carbon dioxide and water. No intermediate compounds are formed in these photochemical oxidations. We have thus been able to imitate successfully the physiological processes of oxidations on which animal life depends.

(4) Voit in his necrology of Pettenkofer writes: "that the metabolism in the body was not proportional to the combustibility of the substances outside the body, but protein which burns with difficulty outside metabolises with the greatest ease, then carbohydrates, while fat which readily burns outside is the most difficultly combustible in the body." We have tried to imitate the metabolism taking place in the animal body and have made comparative experiments⁴ on the oxidation of butter, egg-white, egg-yellow, starch, glycogen, and glucose by passing air at the ordinary temperature in presence of sunlight. The following results have been obtained:

Egg-yellow	60.9%	oxidised
Egg-white	31.25%	"
Starch	38.2%	"
Butter	31.8%	"
Glucose	13.6%	"

^{1, 2} and ³ Palit and Dhar: *J. Phys. Chem.*, **32**, 1263 (1928); **34**, 993 (1930); *Z. anorg. allgem. Chem.*, **191**, 150 (1930).

⁴ *J. Phys. Chem.*, **34**, 993 (1930).

It appears therefore, that egg-yellow is the most easily oxidisable substance in presence of light, then come starch, egg-white, and butter, while glucose is the least oxidisable. Hence eggs which metabolise readily in the animal body, are also easily oxidised by air at the ordinary temperature in presence of sunlight.

(5) We have investigated whether the Einstein Law of Photochemical Equivalence is applicable to the photochemical oxidation of carbohydrates, fats and nitrogenous substances in sunlight. The amount of energy absorbed by solutions of carbohydrates, fats and nitrogenous substances was measured with the help of Boys' radiomicrometer. It is interesting to note that the Einstein Law of Photochemical Equivalence is applicable to the photochemical oxidation of glucose, lactose and α -alanine by air. The law however is not applicable to the photochemical oxidation of glycine by air where about seven molecules react per quantum of light absorbed. These results show that practically colourless one percent aqueous solutions of glucose, lactose, glycine and alanine can absorb light from the sunshine falling on the solutions. This absorption of energy leads to the activation of the molecules and their consequent chemical reaction with oxygen in presence of light. When these solutions are mixed with ferric or uranium nitrate, the absorption of radiation is considerably increased and the amount of oxidation is also increased.

(6) In one of our previous publications,¹ we have shown that appreciable amounts of the compounds of the peroxide type are formed when air is passed through aqueous suspensions of cholesterol, olive oil, butter and many other substances like coconut-oil, castor oil, linseed oil, mustard oil, etc. It has been also observed that olive oil can be retained in that activated or excited state for a sufficient length of time if kept in the dark but this phenomenon was not observed in a marked degree in the case of cholesterol, as it was found to have lost its active or excited state in the course of a few days. Moreover appreciable amounts of glucose have been oxidised by mixing the solution of glucose with the exposed cholesterol, olive oil, butter, and other oils respectively, containing the peroxide compounds. Hence it is believed that the anti-rachitic and beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxide, which help the oxidation of food materials in the animal body. Substances can acquire anti-rachitic properties when exposed to light only in presence of air and light.

In the light of the observations made, we can safely say that when the food materials are exposed to sunlight in presence of air, they take up oxygen forming some peroxide type of compound which can oxidise other food materials when mixed with them. Consequently the addition of the exposed substances to ordinary food stuff facilitates the proper ingestion of food materials and produce efficacious results.

(7) Sunlight and artificial lights have been used with great success in the treatment of tuberculosis, pernicious anaemia, rickets, etc. In some previous

¹ J. Phys. Chem., **34**, 737 (1930); Ind. J. Med. Research, **17**, 430, 993 (1929).

publications¹ we have emphasised the importance of sunlight in the treatment of deficiency diseases and we have observed that rickets, osteomalacia, beriberi, pellagra, etc., would have been more common in poor tropical countries like India and China, had not the compensating agent—sunlight—been present. This conclusion had been corroborated by our experiments on the metabolism of animals.

(18) Having investigated the above facts on the efficacy of exposed oils in oxidising other food materials, we have carried on experiments² on the metabolism of pigeons and rats using these exposed and unexposed oils. Incidentally we have also investigated the influence of sunlight and small quantities of colloidal iron preparations, juice of several green leafy vegetables, tomato, etc. in the metabolism of pigeons and rats. For this, different lots of pigeons and rats were fed on polished Rangoon rice, which is believed to be entirely devoid of vitamins, for about a month. One lot had plenty of sunlight, whilst the other had very little of it. The lot which had sunshine did not show any sign of polyneuritis whilst the other lot, not having sunshine, developed stomachic troubles first and then acute form of polyneuritis, paralysis and their eyes were highly affected. All the affected pigeons were separated from the rest and kept in sunlight and fed artificially with substances rich in vitamins and containing iron in small doses. They were all finally cured and restored to normal health.

In carrying out feeding experiments upon animals, one cannot but realise that the balance between health and disease, even between life and death, is actually under control. The scales are so sensitive that they have been swayed in one direction or the other by the addition or subtraction of seemingly trifling quantities of certain food stuffs. A growing animal provided with plenty of food can be stunted at will, made to decline almost to the point of death and restored with miraculous suddenness by slight readjustment of the diet.

The experiments on the metabolism of animals were further investigated with different lots of pigeons and rats with the addition of following substances mixed with their diet. (Rangoon rice):

1. Rangoon rice and kept in sunlight, (2) Rangoon rice mixed with juice of green leafy vegetables and kept in diffused light, (3) Rangoon rice mixed with irradiated oil and kept in diffused light, (4) Rangoon rice mixed with unexposed oil and kept in diffused light, (5) Rangoon rice mixed with colloidal iron preparation and kept in diffused light, (6) Rangoon rice mixed with a little quantity of Bajra (*Pennisetum typhoideum*) and kept in sunlight and (7) Rangoon rice mixed with a little quantity of gram and kept in sunlight. The experiment lasted for a month. Our experimental results show³ that animals receiving normal diet and sunshine viz. set nos. 6 and 7, keep very

¹ J. Phys. Chem., **32**, 1263 (1928); **33**, 1897 (1929); *Chemie der Zelle und Gewebe* **12**, 217, 225, 317 (1925); **13**, 209 (1926).

² J. Phys. Chem., **32**, 737 (1930); *Ind. J. Med. Research*, **17**, 430 (1929).

³ Palit and Dhar: *J. Phys. Chem.*, **34**, 737 (1930); *Ind. J. Med. Research*, **17**, 430 (1929).

good health. Even if the animals do not get any vitaminous food but only sunlight, they keep good health. Of course, the animals which get irradiated oils were much better than those getting iron preparations and unexposed oils, though they were kept in darkness. Still they were getting inferior in general health to those which obtained sunlight but no vitaminous food. Hence it is found that irradiated oils are not efficacious as the vitaminous food or even as sunlight. It is also found that iron in small doses which are present in green leafy vegetables is beneficial to health. Our results also show that iron in larger doses is rather harmful to animals and cannot prevent the attack of polyneuritis. All these experiments confirm our view that sunlight acts as a promoter of oxidation of food materials in the body, and normal food with plenty of sunlight is the best for the maintenance of health. We are of opinion that in presence of sunlight the metabolism of the food materials taken in the system is accelerated and that is how the disease is avoided. We believe that by absorption of sunlight, the body cells are activated and greater amounts of oxidation of carbohydrates, fats and proteins take place than in the absence of sunlight. It seems pretty generally accepted that several diseases are caused by defective metabolism. We are of opinion that in these diseases which are caused by the want of proper metabolism, sunlight or artificial light should be highly efficacious, because as we have proved experimentally that the oxidation of fats, carbohydrates and proteins is greatly accelerated by light.

All our experiments on slow and induced oxidations as well as on photochemical oxidations are imitations of Nature's process of oxidation and throws considerable light on the processes of life phenomenon.

Further work in this line is in progress in these laboratories.

Summary

(1) An explanation for the mechanism of induced oxidation has been suggested.

(2) Carbohydrates, fats, proteins, food materials, and other organic substances have in presence of inductors been oxidised.

(3) The oxidation of fats is retarded by carbohydrates or less powerfully by proteins and to a greater extent by a mixture of proteins and carbohydrates. Also the oxidation of proteins is markedly retarded by fats and carbohydrates.

(4) The view, that diabetes is due to insufficient oxidation of glucose and fats in the body, has been corroborated by our experimental evidence on the oxidation of insulin, which go to prove that the oxidation of insulin leads to oxidation of glucose in the body. This explains the decrease of glucose in and disappearance of acetone bodies from, the diabetic blood and urine on injection of insulin.

(5) Iron in the blood accelerates catalytically the oxidation of food materials. The iron preferably of colloidal nature, when taken into the system, will supply the natural deficiency and the necessary amount of

oxidation will take place, thus showing the efficiency of the iron preparations in deficiency and metabolism diseases. An explanation that fever is an autocatalytic reaction has also been suggested.

(6) Experimental results on the estimation of carbon dioxide prove that carbohydrates, fats, proteins, and other organic substances are oxidised by air at the ordinary temperature in presence of inductor chiefly to carbon-dioxide and not to any intermediate products.

(7) Comparative experiments on the induced oxidation of fats, carbohydrates, and proteins show that in presence of inductor, the order of oxidation is the same as that obtained by Voit, the eminent physiologist.

(8) An explanation of the internal use of alkali and alkaline carbonates has been suggested based on the increased oxidation of food materials by air in presence of alkali. The alkaline treatment should prove efficacious in gout, diabetes, beri-beri, rickets and other metabolism diseases.

(9) Aqueous solutions or suspensions of the following substances have been oxidised by passing air in presence of sunlight: arabinose, cane sugar, galactose, glucose, lactose, laevulose, maltose, starch, glycogen, urea, glycerine, α -alanine, hippuric acid, sodium urate, potassium stearate, potassium oleate, potassium palmitate, potassium oxalate, sodium formate, sodium tartrate, lecithin, cholesterol, butter, milk, egg-white, egg-yellow, and dilute solutions of citric, tartaric and lactic acids. Zinc oxide, uranium nitrate and ferric nitrate act as a powerful photosensitiser in the above oxidations and in their presence the amount of oxidation in each case is greater than in their absence. Our experimental results show that the amount of oxidation increases with (a) the intensity of light, (b) the amount of light falling on the solutions, and (c) the time of exposure.

(10) Experimental results on the estimation of carbon dioxide prove that carbohydrates, fats, proteins, food materials, cholesterol, lecithin etc. are oxidised by air in presence of sunlight chiefly to carbon dioxide and not to any intermediate product.

(11) Comparative experiments show that order in which the food materials are oxidised in presence of sunlight is as follows: egg-yellow > starch > egg-white > butter > glucose.

(12) The Einstein Law of Photochemical Equivalence is approximately applicable to the photochemical oxidations of glucose, lactose and alanine by air.

(13) Experimental results show that appreciable amounts of the compounds of the peroxide type are formed when air is passed through aqueous suspensions of cholesterol, butter, olive, coconut, mustard, castor, and linseed oils and some carbohydrates. These peroxides have been estimated by the amount of iodine liberated by them from an acid solution of potassium iodide. Moreover appreciable amounts of glucose have been oxidised by mixing the solution of glucose with the exposed substances containing the peroxide compound. Hence it is believed that the anti-rachitic and beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxides which help the oxidation of food materials in the animal body.

(14) From the experiments on metabolism of animals, we have proved that sunlight is the best preventive for disease like polyneuritis, beri-beri, rickets, etc. Olive oil exposed to sunlight and air comes on close second, whereas iron and unexposed oils are harmful to animals. The natural food with plenty of sunlight seems to be the best kind of diet for the maintenance of health. In tropical countries, many deficiency diseases are avoided due to sunlight. Hence sunlight and other kinds of artificial lights prove efficacious in this treatment of diseases specially of metabolic origin.

(15) These results (induced and photochemical oxidations) are very important, because these oxidations are of the same type as those taking place in the animal body. The experiments in this investigation are in reality imitations of Nature's process of oxidation of food materials in the animal body.

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August 27, 1931.*

SOLUBILITY OF SUCCINIC ACID IN BINARY MIXTURES

BY WILDER D. BANCROFT AND F. J. C. BUTLER

Many cases are known of a maximum solubility of a solid in some mixture of two consolute liquids.¹ Holleman and Antusch consider the possible explanations for aqueous alcohol to be: the formation of alcohol hydrates in solution; the formation of complex molecules of the solute in solution; the formation of a compound between solvent and solute. There is no evidence for the existence of alcohol hydrates in solution. If this is the sole cause of the abnormality, the position of the maximum must be independent of the temperature. While the absolute amount of the hypothetical compound will vary with the temperature, the percentage composition at which there is a maximum formation of the compound at any temperature will be independent of the temperature.

We have made a study of the behavior of succinic acid, substituting mass concentrations for the volume concentration used by Herz and Knoch. At 20° they found the maximum solubility at about 35% by weight of water; we find it at about 45% by weight at 40°. Seidell found that the position of maximum solubility of acetanilide in aqueous alcohol was displaced by change of temperature. In these two cases there is therefore no justification in assuming that a compound of acetone and water or of alcohol and water plays any important part. This is what one would have expected anyway from the partial pressure curves of aqueous acetone and aqueous alcohol. There is no evidence from these of any appreciable amount of any hydrate being formed.

There is no evidence for the existence of any appreciable amounts in solution of any compound between succinic acid and water or acetone though the non-existence of such compounds has not been proved. Nobody has even made an attempt to show how the maximum solubility of succinic acid in aqueous acetone could be accounted for on the assumption of polymerization or depolymerization of succinic acid. The explanations suggested by Holleman and Antusch seem therefore to be inadequate.

There is one other factor that has not yet received adequate consideration, namely reversible polymerization and depolymerization of either or both of the solvents. If succinic acid is more or less soluble in monomolecular water than in polymolecular water, the solvent action of the water will change with changing concentration of the water.

Experiments were made on the solubility of succinic acid in binary mixtures of methyl, ethyl and propyl alcohols. The data are shown graphically in Fig. 1. The solubility curves are so near straight lines that any variation from them

¹ Cf. Holleman and Antusch: *Rec. Trav. chim.*, **13**, 277 (1894); Herz and Knoch: *Z. anorg. Chem.*, **41**, 315 (1904); **45**, 262; **46**, 193 (1905); Seidell: *J. Am. Chem. Soc.*, **29**, 1088 (1907); Dehn: **39**, 1399 (1917); Highfield: *Trans. Faraday Soc.*, **22**, 57 (1926); Disselkamp: *Z. physik. Chem.*, **123**, 99 (1926); Angelescu and Dumitrescu: **132**, 217 (1928); Wilson and Wright: *J. Chem. Soc.*, **1928**, 3111; Duff: **1931**, 881, 1196.

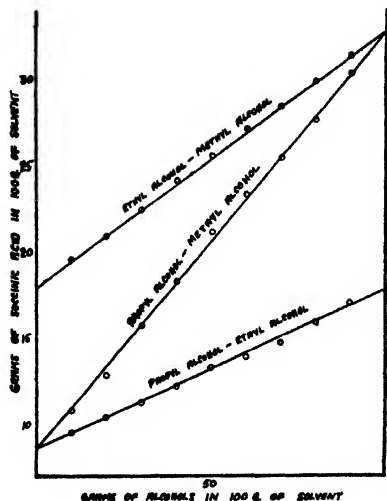


FIG. 1

is a maximum solubility as expected. As might also have been expected there is less of a maximum relatively with aqueous methyl alcohol than with the other pairs of liquids because the relative effect ascribed to monomolecular water will be less the greater the solubility in the organic liquid.

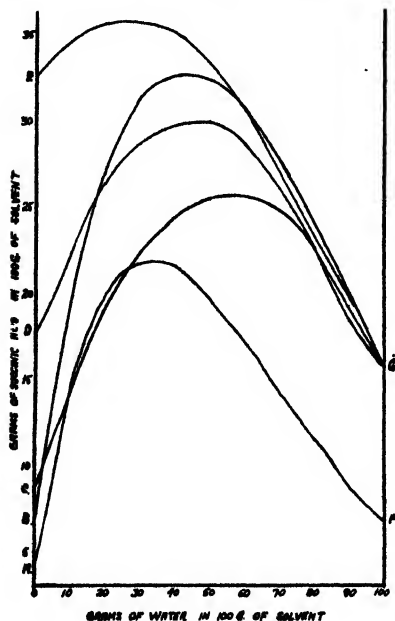


FIG. 2

AF:—Aqueous acetone at 20°
 BG:—Aqueous acetone at 40°
 CG:—Aqueous propyl alcohol at 40°
 DG:—Aqueous ethyl alcohol at 40°
 EG:—Aqueous methyl alcohol at 40°

can be disregarded for the time being. In terms of our hypothesis this means that there is practically no change in solubility of succinic acid with changing polymerization of the alcohols.

Similar data for water with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol are shown graphically in Fig. 2. In all cases there is a maximum solubility and this maximum solubility was predicted from the experiments of Herz and Knoch with aqueous acetone. It seemed probable that other acids of the same type would behave similarly and in Fig. 3 are given the data for adipic acid for water with acetone, methyl alcohol and ethyl alcohol at 40°. In each of the three cases there

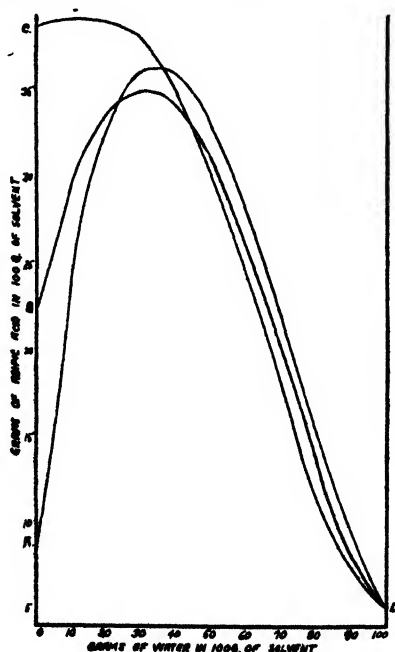


FIG. 3

AD:—Aqueous acetone at 40°
 BD:—Aqueous ethyl alcohol at 40°
 CD:—Aqueous methyl alcohol at 40°

If we make the explicit assumption that the solubility due to an alcohol is a linear function of the concentration in the aqueous alcohol mixtures, just as it has been shown to be in the mixtures of two alcohols, the difference between the calculated value for the alcohol and the found value for the mixture represents the assumed solubility of succinic acid in the water. By recalculating to the basis of one hundred grams of water, we get the data given in Table I.

TABLE I

M = weight percentage of methyl alcohol in aqueous alcohol.
 E = weight percentage of ethyl alcohol in aqueous alcohol.
 P = weight percentage of propyl alcohol in aqueous alcohol.
 x = calculated grams of succinic acid per hundred grams water.
 Temperature, 40°.

M	x	E	x	P	x
0	15.7	0	15.7	0	15.7
10	19.8	10	18.5	10	20.5
20	21.0	20	23.9	20	26.1
30	24.8	30	29.5	30	31.5
40	29.2	40	35.0	40	36.9
50	34.1	50	41.8	50	42.2
60	38.7	60	47.4	60	48.0
70	43.0	70	53.7	70	54.5
80	48.1	80	59.8	80	60.9
90	52.1	90	62.0	90	66.2

TABLE II

M = weight percentage of methyl alcohol in aqueous alcohol.
 E = weight percentage of ethyl alcohol in aqueous alcohol.
 x = calculated grams adipic acid per hundred grams water.
 Temperature, 40°.

M	x	M	x	E	x	E	x
0	5.2	50	21.5	0	5.2	50	41.9
10	4.1	60	28.9	10	6.6	60	51.4
20	4.8	70	36.7	20	11.5	70	63.7
30	8.3	80	40.9	30	19.4	80	76.9
40	14.6	90	42.8	40	28.3	90	94.5

In each case there is a smooth curve with increasing apparent effectiveness as the concentration of the water in the mixture of the two liquids becomes less. Since water is monomolecular in dilute solutions, this means that the apparent solubility of succinic acid in monomolecular water at 40° is approximately four times as great as in pure water at the same temperature. This cannot be the whole truth, however, because the solubilities do not extrapolate to the same value in the three cases. There is therefore another factor to be taken into account and we cannot at present state what that factor is. We

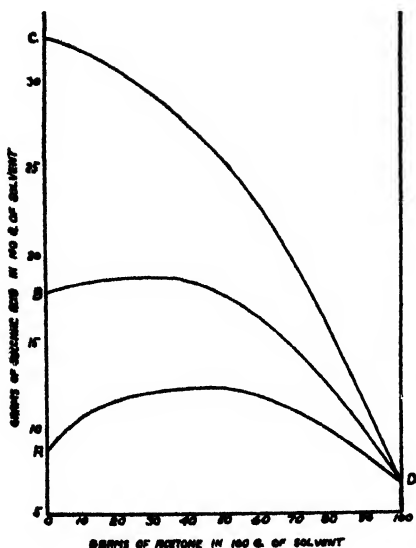


FIG. 4

AD:—Acetone-propyl alcohol at 40°
 BD:—Acetone-ethyl alcohol at 40°
 CD:—Acetone-methyl alcohol at 40°

may point out empirically that the apparent solubility in water comes out lowest in the alcohol in which succinic acid is most soluble. Succinic acid is about twice as soluble in methyl alcohol as in ethyl alcohol and about four times as in propyl alcohol.

A similar result is obtained for adipic acid as shown in Table II.

The general relations are much the same as with succinic acid, but the change in apparent solubility is much greater and the difference between the end values is much greater.

Data for the solubility of succinic acid in mixtures of acetone with methyl alcohol, ethyl alcohol and propyl alcohol are shown graphically in Fig. 4. There is a maximum solubility in acetone and propyl alcohol and in acetone and ethyl alcohol; but none in acetone and methyl alcohol. In terms of our

hypothesis this means that there is a change in the solubility of succinic acid with changing polymerization of acetone. If we assume that the solubilities due to the alcohols are linear functions of the concentration, the apparent solubilities in acetone are given in Table III.

The apparent solubility of succinic acid in monomolecular acetone at 40° is approximately four times that in pure acetone at the same temperature. The apparent solubility is greatest in the propyl alcohol solutions in which

TABLE III

M = weight percentage of methyl alcohol in alcoholic acetone.
 E = weight percentage of ethyl alcohol in alcoholic acetone.
 P = weight percentage of propyl alcohol in alcoholic acetone.
 x = calculated grams succinic acid per hundred grams acetone.
 Temperature, 40°.

M	x	E	x	P	x
0	6.60	0	6.60	0	6.60
10	8.89	10	8.52	10	8.21
20	11.31	20	10.52	20	10.04
30	13.63	30	13.10	30	12.03
40	16.27	40	15.37	40	13.95
50	18.22	50	17.64	50	15.92
60	19.57	60	19.70	60	17.85
70	21.77	70	20.70	70	20.53
80	22.90	80	21.45	80	23.35
90	24.60	90	22.50	90	28.70

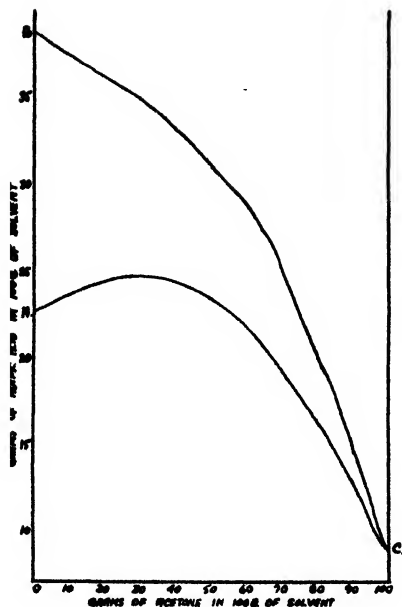


FIG. 5

AC:—Acetone-ethyl alcohol at 40°
 BC:—Acetone-methyl alcohol at 40°

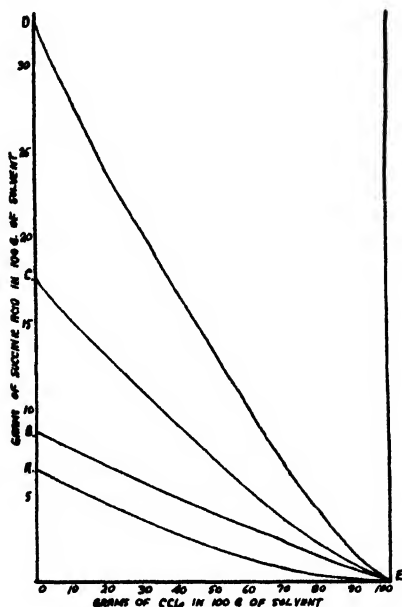


FIG. 6

AE:—CCl₄-acetone at 40°
 BE:—CCl₄-propyl alcohol at 40°
 CE:—CCl₄-ethyl alcohol at 40°
 DE:—CCl₄-methyl alcohol at 40°

the solubility of succinic acid is the least; but it is least in the ethyl alcohol solutions and not in the methyl alcohol solutions, as was the case in the aqueous solutions. No explanation is offered for this discrepancy.

The solubility data for adipic acid in mixtures of acetone with methyl alcohol and with ethyl alcohol at 40° are shown graphically in Fig. 5. There is a maximum solubility in the ethyl alcohol solutions and no maximum in the methyl alcohol solutions. This is qualitatively identical with what was found with succinic acid. The calculated data for the apparent solubilities of adipic acid in acetone are given in Table IV.

The apparent solubility of adipic acid in monomolecular acetone at 40° is three to four times the solubility in pure acetone at that temperature. The

TABLE IV

M = weight percentage of methyl alcohol in alcoholic acetone.

E = weight percentage of ethyl alcohol in alcoholic acetone.

x = calculated grams adipic acid per hundred grams acetone.

Temperature, 40°.

M	x	M	x	E	x	E	x
0	8.71	50	23.22	0	8.71	50	24.08
10	11.94	60	24.83	10	11.74	60	28.05
20	16.00	70	26.07	20	14.98	70	29.53
30	19.00	80	26.50	30	17.96	80	31.55
40	22.65	90	25.80	40	21.05	90	32.90

higher apparent solubility occurs in the ethyl alcohol solutions and adipic acid is less soluble in ethyl alcohol than in methyl alcohol.

Succinic acid is practically insoluble in carbon tetrachloride. Data for the solubility in mixtures of carbon tetrachloride with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol at 40° are shown graphically in Fig. 6. All the curves are slightly concave as seen from above. This is not surprising because carbon tetrachloride would tend to precipitate succinic acid from solution in an alcohol and succinic acid would increase the partial pressure of carbon tetrachloride in an alcoholic solution. This would give a curve which would be concave as seen from above.

The general results of this investigation are as follows:

1. In binary mixtures of methyl alcohol, ethyl alcohol, and propyl alcohol, the solubilities of succinic acid are practically linear functions of the concentrations of the solvent.
2. With binary mixtures of water and the alcohols, water and acetone, and acetone and the alcohols, the solubility curves for succinic acid and for adipic acid, so far as determined are convex as seen from above.
3. There are no maxima in the solubility curves for succinic acid and adipic acid in mixtures of acetone and methyl alcohol. There is a maximum solubility in each of the other curves which are convex when seen from above.
4. The solubility curves for succinic acid in binary mixtures of carbon tetrachloride with acetone, methyl alcohol, ethyl alcohol, and propyl alcohol, are concave as seen from above. The solubility of succinic acid in carbon tetrachloride is practically negligible.
5. If a maximum solubility is due solely to the formation of a definite chemical compound between the two liquids, the concentration at which the maximum solubility occurs must be independent of the temperature.
6. With acetone-water mixtures and succinic acid the concentration showing maximum solubility changes with varying temperature. The existence of a hypothetical hydrate of acetone cannot therefore be the sole factor and is probably not an important factor in causing the maximum solubility in this system.
7. Since the solubility curves of succinic acid in binary mixtures of methyl ethyl, and propyl alcohols are very nearly straight lines, we must assume that the solubility of succinic acid does not vary much with varying polymerization of the alcohols.
8. From the existing data it seems probable that succinic acid and adipic acid are more soluble in depolymerized water and acetone than in the polymerized liquids.
9. Since the calculated values for the apparent solubility of succinic and adipic acids in depolymerized water and acetone vary with the nature of the other liquid, there must be still another factor to be taken into account.
10. In all cases but one the apparent solubility of succinic or adipic acid in depolymerized water or acetone comes out higher the less soluble the organic acid is in the other liquid. No explanation is offered for this.

NOTE ON H. B. WEISER'S AND W. O. MILLIGAN'S PAPER ON THE TRANSFORMATION FROM ROSE TO GREEN MANGANOUS SULFIDE

BY GEORG LANDESEN

In the issue for August of this journal Weiser and Milligan¹ published some investigations on the question mentioned, referring there to the first of two of our papers dealing with the same phenomenon² which, however, is done partly in such a peculiar way, that it calls for some remarks in defense.

Weiser and Milligan assert repeatedly that our calculated results do not follow from our reported observations. These assertions are apparently proved by reproducing part of our Table I³ under the heading of "Table V" on p. 2338 of their paper. This table is accompanied by some calculations that lead Weiser and Milligan to results which differ from those obtained by us. To the reader, however, the true cause of these differences remains hidden, because Weiser and Milligan pass over in silence our statement on the "concentrations of standard solutions" ("Gehalte der Ständigen Lösungen") which we have stated on p. 110 immediately before Table I. There is to be found e.g. a detailed statement of the concentration of the hydrochloric acid which was used for titrations mostly in tenfold dilutions, here as well as in the following Tables II to VI. In headings and headlines of these for the sake of brevity, and on account of proximity to normality resp. 0.1 of normality the concentrations are marked as $n/10$ -HCl-solution for instance. If in the calculations account is taken of this statement of concentration of the hydrochloric acid and its contents of NH_4SH - and NH_3 -solutions per cc as stated in the first and second columns of the tables referred to, then it is evident that the calculated figures cited in these tables are correctly deduced from the reported observations.

To correct but one of the examples calculated by Weiser and Milligan, the apprehended value 14.16 (in the second column of Table I) is obtained by, first, keeping in mind that the quantity of ammonia (0.017 gr in 10 cc of the residue of filtration) equivalent to manganese which was poured into the reaction mixture equals to $0.017 \cdot 10 / 0.0207 = 8.21$ cc if expressed in cc of the tenfold diluted hydrochloric acid mentioned above. In the second place, the quantity of ammonia contained in 10 cc of the reaction mixture, i.e. in 2.5 cc of NH_4SH solution, is equivalent to $8.95 \cdot 2.5 = 22.37$ cc of the same tenfold diluted solution of hydrochloric acid, by the first column of Table I. The difference of these two values leads to $22.37 - 8.21 = 14.16$, i.e. the apprehended value.

Did the circumstance that the reported titrations (in the second column of Table I of our paper, p. 111, under "gef.") gave a higher value than the value 12.37 as calculated by Weiser and Milligan really not suggest to them

¹ J. Phys. Chem., **35**, 2330-44 (1931).

² A. Mickwitz und G. Landesen: Z. anorg. allgem. Chem., **131**, 101 (1923); the other paper being: G. Landesen: **193**, 277 (1930).

³ Z. anorg. allgem. Chem., **131**, 110-111 (1923).

that the cause of their differing values might lie with them? The same applies to all remaining calculations done by Weiser and Milligan to control our figures; and their thoughtless objections are thereby annihilated by themselves.

At the very beginning of their paper on p. 2330 (before and after "(1)", and near the bottom of this page), Weiser and Milligan intimate by unskillful wording in quoting us that we too have proved and concluded that the rose manganous sulfide does not turn green when precipitated by alkali sulfide. In connection therewith they then describe experiments which prove under certain conditions the contrary. But Weiser and Milligan ought to know from our paper that on this subject no investigations were done by us, nor any conclusions drawn.⁴ How misleading their representation is, is shown plainly by the fact that the abstractor of Weiser and Milligan's paper in the "Zentralblatt (1931 II p. 2440) begins with the statement that we have "established" this fact.

Finally, the statement on p. 2335 saying that we have denied the influence of the rate of mixing on the rate of transformation to the green modification as recognised by Fischer, is not correct. When Fischer's statements on this subject are compared,⁵ it is not quite possible to speak of a recognition of this influence. Accordingly, treating the literature on the subject on p. 102 of our paper, we have indicated that Fischer's many contradictory statements do not allow any definite conclusion on this influence which seems not to be essential if other definitive conditions are observed.

*Inorganic Chemistry Laboratory
of University, Tartu-Dorpat,
April 11, 1932.*

⁴ W. M. Fischer, however, whose paper is repeatedly referred to by Weiser and Milligan, but which they seem not to be acquainted with, has made investigations and has drawn definite conclusions on this subject; cf. J. Russ. Phys.-Chem. Soc., 46, chem. section pp. 1496 to 1500, and 1484 (1914).

⁵ Cf. pp. 1485 to 1490, 1492 to 1493 and 1508 to 1510 of his paper under (4).

NEW BOOKS

Annual Review of Biochemistry. Edited by James Murray Luck. Vol. I. 23 × 16 cm; pp. vii + 724. Stanford University, Stanford University Press, 1932. Price: \$5.00. "It is not without significance that the last few years have witnessed the inception of new journals, of interest to chemists, at no less a rate than one every two weeks. . . . It is the exceptional individual who succeeds in reading an appreciable portion of the papers outside the confines of his own restricted field of research. The Annual Review of Biochemistry will present from year to year reviews of the current developments in from twenty-five to thirty of the major fields of interest," p. v.

The articles and authors are: permeability, R. Höber; the rôle of water in the structure and properties of protoplasm, R. A. Gortner; biological oxidations and reductions, R. Wurmser; enzymes, E. Waldschmidt-Leitz; the chemistry of acyclic constituents of natural fats and oils, R. J. Anderson; the chemistry of the sterols, bile acids, and other cyclic constituents of natural fats and oils, A. Windaus; the chemistry of the lipins, I. Smedley-MacLean; the chemistry of the amino acids and the proteins, C. L. A. Schmidt; the chemistry and metabolism of the compounds of sulfur, H. B. Lewis; the chemistry and metabolism of the compounds of phosphorus, H. D. Kay; the chemistry of the carbohydrates and the glucosides, P. A. Levene and A. L. Raymond; carbohydrate metabolism, P. A. Shaffer and Ethel Ronzoni; fat metabolism, W. R. Bloor; the metabolism of proteins and amino acids, J. M. Luck; nutrition, A. H. Smith; vitamins, L. H. Harris; the hormones, D. L. Thomson and J. B. Collip; the chemistry of muscle, J. K. Parnas; liver and bile, J. L. Bollman and F. C. Mann; the metabolism of brain and nerve, E. G. Holmes; chemical embryology, Joseph Needham; the chemistry of the animal pigments, Hans Fischer and F. Neumann; plant pigments, A. E. Mirsky and M. L. Anson; the terpenes, saponines, and closely related compounds, L. Rusicka; the nitrogenous constituents of green plants, H. B. Vickery; mineral nutrition of plants, D. R. Hoagland; the chemistry of the bacteria, M. Stephenson; immunochemistry, Michael Heidelberger; the biochemistry of the fungi, N. N. Iwanoff.

"Mammals and teleosts are characterized by low figures [for the time of hemolysis,] elasmobranchs and amphibia by high values; reptiles give hemolytic times somewhat higher than mammals, and the birds show a peculiar behavior inasmuch as the value for the chicken is high, while those of the pigeon and duck are low. . . . In mammals permeability to urea is much greater than to ethylene glycol; the reverse is true for elasmobranchs and teleosts. Reptiles resemble mammals; birds and amphibia approach the fishes. The comparison between urea and glycerol gave similar results. The penetrating faculty of urea exceeded by far that of glycerol in the case of mammalian cells, and to a somewhat smaller degree in reptiles and the frogs, while the permeability of the two substances is about the same in fishes," p. 2.

"Lepeschkin has published new experiments regarding the influence of light upon cell-permeability. He investigated the speed of penetration of methylene blue into the leaves of *Elodea* with a colorimetric method especially worked out for *Elodea*. The permeability increases in the light and decreases in the dark. It may be objected: (1) that the difference in coloring may be produced by a change in the adsorption of the dye in light—but dead cells adsorb dyes with equal velocity in the light and in the dark; or (2) the affinity of the cell sap may be increased by the illumination—but also the amount of dye adsorbed by the cell is the same in light and dark. By shading a part of the leaf by means of a strip of tin-foil it can be demonstrated that the increase of permeability does not spread to neighboring cells. The greater the change of the illumination—in positive and negative direction—the greater is the change of permeability; this can be explained by the supposition that there exist in the cells substances essential for permeability, destroyed by light and restored in the dark; therefore, the more products of the decomposition the protoplasm

contains, the more rapidly the restoration proceeds, and conversely. The rays most active are those with a wave-length of 320 to 420 $m\mu$," p. 16.

"In the case of gelatin all of the water which would freeze was frozen when the temperature was lowered to -6°C . and no additional water froze even when the temperature was lowered to -50°C ," p. 23.

"McQuarrie has made the important discovery that at least certain types of epilepsy appear to be due to disturbed water relationships and that when water is withheld from the patient the patient becomes free from seizures and may remain entirely free from seizures providing that the water intake is reduced to a minimum. A sudden increase in the water intake or the parenteral administration of a solution of the pituitary or the anti-diuretic hormone of the hypophysis produces a positive water balance in such 'dehydrated' patients and a corresponding recurrence of the seizures. If, however, sufficient urea is added to the ingested water, the seizures do not develop," p. 32.

"Harding and Harris report that in order to produce convulsive spasms in dogs the retention of water must exceed 60 cc. of kg. of body weight and that, while the administration of 10 percent NaCl solution will cause recovery, the administration of hypertonic urea solutions is relatively ineffective. These authors express doubt that the convulsions of epilepsy and eclampsia are due to water intoxication even though they may be accompanied by a positive water balance," p. 35.

"Frog skin shows a differential directional osmosis which is reversed as one passes the isoelectric point," p. 44.

"It is shown by the recent researches of Meyerhof and Lohmann on the extract from muscles of cold-blooded animals, that during the esterification of the phosphate which precedes the scission of glucose into lactic acid the adenylyl-pyrophosphate, which is the coenzyme of this transformation, undergoes scission. The resynthesis of phosphagen in anaerobiosis is rendered possible by the energy of scission of this adenylyl-pyrophosphoric acid, while the energy of formation of the lactic acid serves to reconstitute the decomposed pyrophosphate. Under conditions of aerobiosis the chain of energy-transfer, which makes possible the resynthesis of glycogen from the lactic acid, and in part of the phosphagen, is still longer, and is yet incompletely known," p. 56.

"Bamann and Laeverenz have shown that in splitting racemic esters of the mandelic acid group by liver esterase, a reversal of the optical selectivity can be obtained by adding strychnine; the rotatory direction of the more quickly saponified component of the racemate was found to be different with and without strychnine. Later researches have developed this observation. The change in steric specificity under the influence of the alkaloid has proved, within the limits tested, to be independent of the degree of purity of the enzyme from the accidental and separable concomitant materials of the enzyme preparations; there seems to be a reaction of the strychnine with the enzyme itself," p. 71.

"Oparin and Kurssanow have reported on the important observation of an enzymatic synthesis of cane sugar. Having found that the transformation of γ -fructose $<2,5>$ present in cane sugar into β -fructose $<2,6>$ which takes place after its hydrolysis, is retarded by phosphorylating the cane sugar, they succeeded by simultaneous action of saccharase and phosphatase on solutions of invert sugar in the presence of phosphate, in obtaining a synthetic sugar identical with cane sugar," p. 80.

According to Lohmann the presence of magnesium ion as well as of co-enzyme is necessary for fermentation by dry yeast. The conjoint action of the magnesium is responsible for the partial process of glucose-phosphorylation since the activity of the phosphatase can, it is well known, be much increased by magnesium ion," p. 82.

"Rosenfeld found from feeding experiments on hens that lecithin could be formed in the body if phosphorus and fatty acids were supplied. When glycine was added to a basal diet containing ether-extracted casein, starch, sugar, stearic acid, and salts, the quantity of lecithin formed in the body was much increased. Rosenfeld therefore regards glycine as a forerunner of lecithin," p. 137.

"Recent studies on the colloidal properties of lecithin have been especially concerned with two questions, (a) the mutually antagonistic effect of solutions of lecithin and chole-

sterol; and (b) the effect of the addition of lecithin on the precipitation of serum proteins. Theorell and Widström have confirmed the antagonistic action of lecithin and cholesterol on the haemolysis of red blood corpuscles," p. 139.

"In 1920, Meigs, Blatherwick, and Cary described experiments on the mammary gland which seemed to offer conclusive evidence that milk fat was derived from phospholipins, for the blood left the gland richer in inorganic phosphate and poorer in phospholipin in comparable amount. Jost has now brought forward further evidence in support of the view previously advocated by Leathes that the phospholipins act as intermediate substances in fat metabolism," p. 144.

"It is strongly suspected that they [Bancroft and Barnett] have not taken into account all of the factors which must be considered in the reactions which they were studying," p. 164.

"A very interesting dismutation of glyceric aldehyde was observed by Strain and Spoehr. These authors found that glyceric aldehyde is readily converted by organic amines into methylglyoxal which was identified as its *m*-nitrobenzoyl osazone. The reagent was added to the reaction mixture and the osazone settled out in course of the reaction. Glyceric aldehyde does not form an insoluble osazone. Dihydroxyacetone does not undergo dismutation under the same conditions," p. 227.

"The chief result of the new facts is the removal of lactic acid from the central rôle it has long been supposed to occupy, wherein the energy of its formation was the source of the work of contraction. With the demonstration by Lundsgaard that frog muscle when poisoned with iodo- or bromo-acetic acid contracts normally for a time without formation of lactic acid, Meyerhof and Hill were at last forced to agree with the contention of Embden, reiterated since 1924 (Lehnartz), that a part—and now all—of the lactate is formed after the contraction is over. So all the fine balance sheets heretofore thought to demonstrate a quantitative time-energy relation between the initial heat of contraction and lactic-acid formation from glycogen must now be set aside. The idea of a chemical coupling of the various reactions set off by stimulation, never very clearly defined but always implied, now seems impossible since the reactions are separate in time, and Meyerhof now regards the relations as only energetically coupled through cellular activity. Hahn (1931) has criticized this concept," p. 248.

Adrenalin retards the adsorption of sugar by the peripheral tissues and continuous injection of adrenalin with glucose virtually abolishes sugar oxidation as indicated by the R.Q., p. 253.

"The relation of cholesterol to water balance with its effect in epilepsy and other conditions has received attention. Robinson, Brain and Kay found that in the preconvulsive period in epileptics the cholesterol level in both blood and plasma falls and the seizure takes place at or almost at the lower point in the curve. Incidentally they find that the blood cholesterol is reduced in normal individuals by exercise but comes back promptly. They mention that it is low at the menstrual period, which corresponds to the times of most frequent epileptic attacks," p. 290.

"Mattick and Buchwald found that the cholesterol is higher in plasma than in whole blood in 85 percent of cancer patients. In 80 percent of normal it is higher in whole blood," p. 291.

"Apparently the herbivorous animal forms milk fat largely from carbohydrate and has difficulty in using the fat of the food directly for that purpose, while the carnivorous animal can use food and stored fat directly," p. 293.

"Frogs poisoned by injection of 40 mg. of iodoacetic acid or bromoacetic acid become completely rigid after one hour; but if their sciatic plexus be severed before poisoning, the limbs will appear normal after one hour, while the innervated extremities will be rigid. When nerve-muscle preparations from such frog limbs are stimulated, 60 to 100 twitches are produced, which could not be told from normal contractions by their mechanical, thermal, and electrical [Henriques and Lundsgaard] responses (Stage I). Then, the contractions become weaker, and a contracture begins to appear (Stage II), finally the twitches come to an end, and contracture develops rapidly; after a few minutes the muscle is in full rigor (Stage III). *During all these changes no lactic acid is produced in the muscle, either during the periods of activity or when rigor develops.* This is the portentous discovery by Einar Lundsgaard," p. 443.

"We must assume now, with Lundsgaard, that the cleavage of phosphocreatine is the primary change in the normal contraction, as it is the primary and final change in the anaërobic twitch of the iodoacetic muscles; and that this change is followed, in the normal muscle, by restitution of phosphocreatine, depending on the chemical changes of the anaërobic recovery, viz., lactic-acid formation from glycogen and the splitting off of phosphate from the pyronucleotides," p. 445.

"By X-ray investigation, Hopff and Susich have established the identity of the hydrocarbons of balata and gutta-percha, which differ from caoutchouc hydrocarbon. Stillwell and Clark, as well as Hauser and Susich, have observed two modifications of gutta-percha hydrocarbon, having a transition point at 68°," p. 605.

"The rôle of phosphate in lactic fermentations by *Bact. casei* has now been further elucidated (Virtanen and Tikka). It appears that, whereas live cultures of the organism change glucose to lactic acid quantitatively (glucose→hexose monophosphoric ester ["Robison" ester]→lactic acid [100 percent], with dried preparations of the organism 50 percent only of lactic acid is obtained, the remaining 50 percent being found as phosphoric esters," p. 642.

"As may be seen from the works mentioned above, the theories of organic acid formation have entered the stage of vast generalization. The obtaining of succinic, fumaric, and citric acids from acetic acid and alcohol shows definitely that we may accept a uniform schema of sugar metabolism for yeast, as well as for mould fungi, in which, after the breakdown of the sugar has been carried to acetaldehyde, in some cases (yeast) ethyl alcohol is formed, in other cases (through acetic acid or through ethyl alcohol) compound organic acids, such as succinic, fumaric, citric, and other acids, appear. The comprehension of the origin of these acids, as well as of their frequent simultaneous presence, a fact pointing to their common origin, is considerably facilitated. Two courses adopted in research have proved productive; the first, alteration of the cultural conditions (pH, concentration of sugar, amount of nitrogen), with the formation, by the same fungus species, of certain acids and the suppression of others; the second, the study of the various fungi, as well as of their races, with considerable differences in the nature of the acids being formed. The comparison of all data obtained from the two lines of investigation will afford a clear picture of the genesis of organic acids in fungi," p. 689.

Wilder D. Bancroft

Industrial Chemical Calculations. By O. A. Hougen and K. M. Watson. 23 × 16 cm; pp. vii + 502. New York: John Wiley and Sons. London: Chapman and Hall, 1931. Price: 28 shillings. Any manufacturing process in which a material is subjected to a change of physical state or chemical composition properly belongs to the domain of chemical engineering. A chemical engineering process possesses two aspects: an internal or chemical aspect, in which it is displayed as a reaction between certain molecules or ions exhibiting definite quantitative stoichiometric and energy relationships, and an external or engineering aspect in which it appears as an assemblage of special plant units and equipment that are necessary to contain the reaction mass and provide scope for its physical or chemical transformation.

The present book deals with the application of physico-chemical principles to what might be called the "internal design" of a process—the control of a process by a nice adjustment of composition and of pressure and temperature. In so far as chemical engineering is concerned with the control of chemical reactions and physical changes on a large scale, it is very largely applied physical chemistry.

The present book contains much more than is apparent from the title. It is concerned essentially with the application of physico-chemical principles to the control of chemical reactions and physical changes under industrial conditions. The method of presentation adopted throughout the book is admirably clear and logical. Each subject is introduced with a good account of the underlying theory. The industrial conditions to which the theory is to be applied are described and the methods by which the theory can be applied

to the solution of definite problems are demonstrated. To each section is appended a list of well-arranged problems, possessing an authentic industrial flavour, for a student to work out for himself.

After a preliminary discussion of the use of the molal method of calculating the quantities of reaction materials and the way in which these quantities change as a result of chemical interaction, the authors proceed to give a very good account of the kinetic theory of gases, and show how the theory can be applied to the calculation of the volume and density of gases at high pressures and the heating effects resulting from compression and expansion. Further calculations deal with the way in which the composition of a gas mixture changes as a result of chemical reaction.

Succeeding chapters deal in a similar way with evaporation and condensation, with solution and crystallisation, with specific heats and latent heats, with heats of reaction and heats of solution, and more particularly with the thermochemistry of combustion.

Two chapters deal very fully with the preparation of quantitative balances of the materials and energy used in a chemical process. This portion of the book is very well illustrated by a detailed analysis of both materials and heat balances for such typical industrial processes as those of the gas producer, the coal-fired boiler furnace, the gas-fired kiln, the sulphuric acid plant considered section by section and also in its entirety, and the blast furnace. An excellent chapter deals with the calculation of distillation equilibria. The final chapter is devoted to problems involving reaction equilibria.

The book is of the greatest possible value to every student of physical chemistry. It is unfortunate that this subject is often taught by specialists who do not appreciate its industrial significance and utility, particularly as so large a proportion of their students will depend for their livelihood upon applied rather than theoretical physical chemistry. The use of this book, along with the ordinary textbooks of physical chemistry, would do a great deal to "lend an air of verisimilitude" to what is apt at times to be "a somewhat bald and unconvincing narrative."

To the student of chemical engineering, the book is indispensable; in so far as his work is applied physical chemistry, he must be thoroughly familiar with the principles and methods that are so well described in it. Every industrial chemical process is at heart a series of physical and chemical reactions, and, unless he understands the physical chemistry of the process, he is unlikely to be able to deal successfully with the engineering aspect of it.

W. E. Gibbs.

Glastechnische Tabellen: physikalische und chemische Konstanten der Gläser. Edited by Wilhelm Eitel, Marcello Pirani and Karl Scheel. 28 × 20 cm; pp. xii + 714. Berlin: Julius Springer, 1932. Price: paper 145 marks; bound 149.80 marks. The publication of Hovestadt's "Jena Glass" at the beginning of the century brought into a single compass practically all the data on the physical properties of glass known at that time; and the work of Schott, Winkelmann and others associated with the Jena school was responsible for the bulk of those data. It was a proud record to be associated with an industrial concern. From that time onwards, however, for more than a decade, little new fundamental work on glass appeared save that on general theory inspired by G. Tammann. Even in Germany no institution of advanced learning realised what an opportunity there lay in the study of glasses as a field for systematic investigation. It was left to 1915 for a University in England to embrace this opportunity. Moreover the War stimulated efforts in glass making in a number of countries, efforts which, in America, Japan and Russia as well as in this country were supported by much valuable research work. In 1916 the Society of Glass Technology was founded; in 1917 a Glass Division of the American Ceramic Society; the Deutsche Glastechnische Gesellschaft was founded in 1923. The activities of all these bodies backed by a number of research institutions have developed a distinct science of Glass Technology. Especially in England and Germany has enthusiasm run high. On the literary side, in the compilation of text-books and summaries of knowledge the German workers have been particularly active. The work under review, which owes its appearance in large measure to

the support of the Deutsche Glastechnische Gesellschaft, is the result of one of the most ambitious of these literary projects. It is an attempt to combine with the older data the out-pouring of the past fifteen years and to summarise in a single volume all the known physical and chemical data concerning glasses. Such a summary must be regarded as of value, beyond the immediate service to the glass manufacturer; for glass is to the chemist and physicist a material of fundamental importance, though not always used in the past with due regard to its limitations. With this work of reference available chemists and physicists should be able to obtain a clearer understanding of the service which glass can give and what it cannot give.

The book comprises some 726 pages and consists of a preface, recounting the origin and reason for the book, an introduction explaining the plan of arrangement, and a one page note to the reader explaining how he may utilise the book in designing a glass for a specific purpose.

The systematic portion of the book is divided into three parts. Part I, comprising 88 pages, deals with the properties of the individual oxides such as silica, boric oxide, arsenious oxide, and so on, utilised for all types of glasses, and the phase equilibria in systems of 2, 3, 4 or more of such oxides. The equilibrium diagrams are reproduced in all essential detail together with tables showing the phases present at different temperatures and in some cases drawings of the crystal forms which are deposited. In all cases the latest equilibrium diagrams are given but with selected references to the most important of the older literature. Part II, comprising 536 pages, reproduces in tabular form and in many instances diagrammatically, occasionally also photographically, the records of all modern measurements which have been made on the physical properties of glasses including viscosity, surface tension, internal stress, annealing and softening temperatures, density, elasticity, compressibility, tensile strength, hardness, brittleness, permeability to gas, gas absorption and evolution, thermal expansion, specific heat, heat conductivity, dielectric constant, electrostriction, impact strength, electro-motive force, magnetic susceptibility, refractive index, photo-elasticity, Kerr's constant, Verdet's constant, spectral transmission, U. V. transmission, ultra-red transmission, general transmission, light diffusion, chemical durability and devitrification.

The collation of all these results has been done very well. One sees from them not only what information is available, but also the gaps which remain to be filled and they, therefore, indicate useful fields for further work. The comprehensive section on the durability of glass serves to illustrate both the tremendous diversity of methods which have been employed, and also the very great need for the standardisation of methods so that the results of different investigators can be usefully compared with one another.

The composition of the glasses is not given in Part II, as this would involve needless repetition in many cases. A reference is given in each case, however, to the section in Part III where the composition of any particular glass can be found. In Part III all the glasses which have been referred to in Part II are systematically classified according to their chemical composition. Included is a reference also to organic glasses which in recent years have been studied in connection with the theory of the vitreous state by quite a number of workers.

The whole work has been done uncommonly well. In a systematic examination of the volume the writer has found little or nothing to criticise. The type is beautifully clear and the numerous diagrams, some 900, are not only clear but in some cases appear to better advantage than in the original papers. The work reflects very great credit on the editors, and on the seventeen collaborators who have worked through the very large amount of modern literature.

We may reasonably anticipate that Glastechnische Tabellen will constitute the standard work of reference for all those who are interested in the physical properties of glasses.

W. E. S. Turner

THE TERNARY SYSTEM, K_2SiO_3 - Na_2SiO_3 - SiO_2

BY F. C. KRACEK

The equilibrium phase relations in the ternary system of silica with the two important alkali oxides, Na_2O and K_2O , have not been previously subjected to a systematic study. The knowledge of the phase relations in this system has a bearing on petrology, since the two alkali oxides, Na_2O and K_2O , are important constituents of the common silicate minerals occurring in rocks; the system is also of some interest in glass technology, the three components of the system entering in varying amounts into the composition of commercial glasses. From another point of view the phase relations in this system are of theoretical interest especially in that the results of the present work establish a unique type of solid solution sequence between the two disilicates, $K_2Si_2O_5$ and $Na_2Si_2O_5$.

The component-binary systems, K_2SiO_3 - SiO_2 and Na_2SiO_3 - SiO_2 , have already been published from this Laboratory.^{1,2,3} The information given in the papers quoted must be considered together with the additional data published in this paper in arriving at the correct representation of the phase relations in the ternary system.

The reader is referred to previous papers from this Laboratory for descriptions of the methods, apparatus, and technic employed in the somewhat specialized field of silicate research. No attempt is made in this paper to describe the experimental technic in more detail than is needed to make each point at issue clear.

Preparation of Materials

The mixtures studied were prepared in the form of glasses from Na_2CO_3 , K_2CO_3 and quartz. The Na_2CO_3 used was obtained by dehydration of exceptionally pure $Na_2CO_3 \cdot H_2O$. The K_2CO_3 was derived from $KHCO_3$, also of high purity. The quartz was taken from the special stock of this Laboratory, containing certainly less than 0.05 per cent impurities.

The compositions were made up by heating mixtures of weighed amounts of the reagents, according to a definite procedure. Platinum crucibles were used throughout. Experience has shown that the best results are obtained when the mixed reagents are allowed to sinter slowly at as low a temperature as possible for the reaction to proceed, usually not above $700^\circ C$. Most of the CO_2 is driven off quietly when this is done, and mechanical losses due to bubbling or spattering are completely eliminated. When a large number of mixtures is being prepared, it is best to conduct the sintering in individual, controlled furnaces, allowing about 24 hours for the process. The crucible and

¹ Kracek, Bowen, and Morey: *J. Phys. Chem.*, **33**, 1857 (1929).

² F. C. Kracek: *J. Phys. Chem.*, **34**, 1583 (1930).

³ Morey and Bowen: *J. Phys. Chem.*, **28**, 1167 (1924).

contents are then weighed to estimate the amount of CO_2 still undisplaced. About 99 per cent of the total CO_2 should be expelled before proceeding to the next stage of the heating. The temperature is now raised slowly to drive off the rest of the CO_2 . There should be no frothing of the melted glass, otherwise mechanical losses are unavoidable. In addition to the mechanical losses, there may be losses occasioned by the vaporization of the undissociated carbonates with the escaping CO_2 . After the CO_2 is displaced, the temperature may be raised to 1200°C or higher for a brief period to facilitate diffusion in the molten mixture. It is essential to note that CO_2 -free mixtures lose very little Na_2O or K_2O by volatilization even at moderately high temperatures.

After the first melting the glass is crushed, thoroughly mixed, and replaced in the furnace for a second melting. The process is repeated until no inhomogeneity can be detected in the glass when examined under the microscope, using an immersion liquid matching it in refractive index.

Control of the Composition of the Preparations

During the preparation of the mixtures record is kept of the weights at each stage of the process. It is assumed here that no SiO_2 is volatilized. Kracek showed² that the volatility of Na_2O from Na_2O - SiO_2 mixtures containing more than 60 per cent SiO_2 is negligible when an exact procedure is being followed. The volatilization losses in the preparation of the K_2O - Na_2O - SiO_2 mixtures in the present work were generally of the order of 0.1 to 0.3 per cent, and the assumption is being made that the losses were due solely to the volatilization of K_2O .

A number of the synthetic compositions were checked by direct analysis. Owing to the difficulties inherent in the separate determination of sodium and potassium when both are present in the same sample, the Na/K ratio can be determined with only moderate precision. It was found that the compositions as established by synthesis were correct to within the uncertainty of the analyses, which was of the order of 0.5 per cent on duplicate samples.

The compositions given in the tables are for this reason the synthetic compositions in all cases. This procedure is assumed to be justified further by the general concordance of all the results leading to the derivation of the liquidus surfaces presented in Figs. 1 and 2. The assumption made, that all the volatilization losses are due to K_2O , is definite, and the systematic errors thus introduced into the diagram are well within the experimental error of the analytical determination; they are of major importance only in the sense that a slight distortion of the fields in the region of equimolar Na/K ratio may be produced. For example, let us assume that as much as 0.5 per cent volatilization loss is encountered with a hypothetical synthetic mixture represented by 25 per cent K_2O , 25 per cent Na_2O , and 50 per cent SiO_2 . If we assume that K_2O and Na_2O have equal volatilities the composition of the mixture would be 25.25 per cent K_2O , 24.75 per cent Na_2O , and 50 per cent SiO_2 . The actual composition of the mixture would certainly lie between the two limits, and most probably nearer the 25:25:50 ratio, since K_2O is distinctly more

volatile than Na_2O . Analysis can not decide between these possibilities; it is hence assumed, barring large accidental errors, that the compositions given in the tables are correct to within a maximum *systematic* error of 0.3 per cent.

Liquidus Determination

The "quenching" method of liquidus determination, generally employed in silicate work in this Laboratory, has been used with all the preparations studied in this investigation.

The individual preparations were first crystallized by appropriate heat treatments; the crystal aggregate was then powdered and well mixed to further insure good homogeneity of the preparation, and was then used in the quenching work to determine the liquidus. The quenching furnace control was thermostatic to within $0.5^\circ C$. The temperatures were read by calibrated Pt vs. Pt-Rh (10% Rh) thermocouples in connection with the temperature scale of this Laboratory.⁴ A Wolff-Feussner potentiometer with a highly sensitive galvanometer was used in the temperature measurements, all necessary precautions being observed.

Compositions in the K_2SiO_3 and Na_2SiO_3 fields crystallize readily. In the disilicate fields, *i.e.*, $K_2Si_2O_5$ and $Na_2Si_2O_5$, a variety of behavior is encountered. In general, those preparations whose compositions contain more K_2O or Na_2O than is required to yield a disilicate can be crystallized with ease in the dry state. Preparations with more SiO_2 than is required for a disilicate can usually be crystallized in the dry way only if the liquidus lies above 750° , or if they lie near the disilicate join. When a much larger excess of SiO_2 is present, crystals will not grow even in seeded preparations in the dry state if the liquidus is much below 750° , and hydrothermal crystallization must be employed.^{1,5,6} Similar considerations apply to the fields of $K_2Si_4O_9$ and of quartz. Tridymite can usually be crystallized from the mixtures in which it forms the stable phase, without any particular difficulty, in the dry way, if sufficient time is allowed; it is to be noted, however, that there is a preponderant tendency for cristobalite to be formed at first, and sufficient time must be given in the initial crystallization to convert the (metastable) cristobalite to tridymite.

Since diffusion in the more or less viscous vitreous melts is not very rapid, enough time must be given each preparation in the melting point experiments to come to equilibrium before quenching. One hour or less suffices for the attainment of equilibrium at or near the liquidus temperature in the K_2SiO_3 , Na_2SiO_3 , and certain portions of the $K_2Si_2O_5$ and $Na_2Si_2O_5$ fields. In general when the SiO_2 content lies between 60 and 75 wt. per cent, very much greater length of time must be allowed for the attainment of equilibrium, the time required increasing inversely with the liquidus temperature. When the

⁴ Intern. Crit. Tables, 1, 57; Day, Sosman, and Allen; Carnegie Inst. of Washington, Publ. 157.

⁵ Morey and Fenner: J. Am. Chem. Soc., 39, 1173 (1917).

⁶ Morey, Kracek, and Bowen: J. Soc. Glass Tech., 14, 149 (1930).

liquidus temperature lies below 700°C at least 6 to 12 hours must be allowed; in the quartz field a time of 48 hours or more often fails to dissolve the larger grains. Tridymite dissolves more promptly, and usually 2 to 5 hours are sufficient to reach equilibrium.

It is obvious that dynamic methods of liquidus determination are not applicable to materials of this type. The "quenching" method,⁷ more accurately described as a static equilibrium method, when applicable, can give information not only about the liquidus or other transformation temperatures, but also with regard to the nature of the phases present at equilibrium. The principal requirement of the method is that nucleation of new crystals should be sufficiently slow so that the sample can be chilled to room temperature (by quenching in a non-reacting liquid when necessary) while retaining the structure reached during the thermostatic heating at the desired temperature. The sample is then examined under the microscope to determine whether crystals are present, and their character. By varying the temperature, the limits between which the sample exhibits one phase or another can be fixed as closely as desired. The great advantage of the method lies in the fact that the thermostatic heating at each temperature can be prolonged until equilibrium is attained in the sample.

The Experimental Results

It has been customary to present the results of phase rule studies on silicates from this Laboratory in the form of a more or less abbreviated record of the actual quenching experiments performed.

In view of the large number of preparations studied in this work, and the relative simplicity of the system (there being no ternary compounds), it is deemed advisable here to present the results in a briefer form. The tables following present the synthetic compositions of the mixtures, the equilibrium transformation temperatures, and the temperature interval within which the transformation temperature is located. Thus, if the liquidus temperature is given as 764° , interval $+3-2$, it is meant that the preparation when quenched from 767° was all glass, and when quenched from 762° it contained crystals. Since the thermostatic control of the furnace is accurate to 0.5° , the limits 767° and 762° are intended to denote that these temperatures are known to the nearest 0.5° of the values given; the interval then denotes the limits within which the transformation was determined, and not the uncertainty of the temperature measurement.

The data are given in Table I. In constructing the ternary diagrams, Figs. 1 and 2, use was made of the already mentioned results on the component-binary systems, $\text{K}_2\text{SiO}_3\text{-SiO}_2$ and $\text{Na}_2\text{SiO}_3\text{-SiO}_2$,^{1,2} together with the work of Kracek on the cristobalite liquidus.⁸

⁷ Originally described by Shepherd and Rankin: *Am. J. Sci.*, **28**, 308 (1909).

⁸ F. C. Kracek: *J. Am. Chem. Soc.*, **52**, 1436 (1930).

TABLE I
Compositions and Liquidus Temperatures of Preparations studied
Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K ₂ O	Na ₂ O	SiO ₂				
A. Solid Phase: Na ₂ SiO ₃							
574	—	50.82	49.18	1089	+0.5-0.5	1	CG
2	10.7	41.5	47.8	1009	+4-4	1	C
3	17.7	36.2	46.1	963	+3-3	1	C
4	24.6	31.3	44.1	912	+3-3	3	G
5	32.0	24.5	43.5	858	+4-4	2	G
6	39.1	18.7	42.2	842	+4-4	2	G
7	42.3	15.8	41.9	759	+4-4	3	G
8	38.6	16.7	44.7	780	+5-5	3	G
9	34.9	17.5	47.6	754	+2-2	2	G
10	37.1	13.9	49.0	682	+4-4	3	C
11	26.9	19.4	53.7	729	+2-2	2	CG
12	25.0	17.7	57.3	672	+4-4	3	CG
13	22.3	23.2	54.5	788	+3-3	2	G
14	20.1	20.9	59.0	689	+4-4	4	C
15	14.6	29.4	56.0	847	+4-4	3	C
16	13.1	26.9	59.9	765	+3-3	2	C
17	8.0	31.3	60.7	796	+3-3	2	C
B. Solid Phase: Na ₂ Si ₂ O ₅							
21	—	34.05	65.95	875	+0.5-0.5	2	C
22	3.8	31.1	65.1	827	+2-2	2	C
23	7.2	28.6	64.2	789	+3-3	2	C
24	9.5	26.8	63.7	758	+1-2	2	C
25	12.1	24.8	63.1	739	+3-3	2	C
26	15.8	21.9	62.3	730	+2-2	4	C
27	18.8	19.7	61.6	723	+1-1	12	C
28	22.8	16.5	60.7	711	+3-3	12	C
29	23.9	17.1	59.0	695	+2-2	12	C
30	12.5	25.9	61.6	729	+1-1	12	C
31	7.8	29.9	62.3	776	+2-2	3	C
32	7.0	27.2	65.8	792	+2-2	6	C
33	6.6	25.8	67.6	787	+1-1	6	C
34	6.2	24.5	69.3	780	+1-1	8	C
35	3.7	26.4	69.9	808	+2-2	6	C
36	5.8	22.7	71.5	755	+1-1	10	C
37	11.2	23.0	65.8	753	+1-1	8	C
38	10.5	21.4	68.1	751	+1-1	12	C

* The symbols G, C, B denote that the material used for the quenching experiments was G glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE I (Continued)
Compositions and Liquidus Temperatures of Preparations studied
Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K ₂ O	Na ₂ O	SiO ₂				
39	9.8	20.1	70.2	735	+2-2	10	C
40	14.1	18.5	67.4	726	+2-2	8	C
41	21.5	15.2	63.3	707	+2-2	8	C
42	19.9	14.2	65.9	679	+4-4	16	B
43	18.9	13.3	67.8	649	+2-2	8	B
44	18.2	13.1	69.7	638	+2-2	24	B
45	21.6	9.6	68.8	597	+3-3	24	B
115	9.1	18.9	72.0	723 m	+3-3	6	C
117	5.3	21.7	73.0	741 m	+3-3	6	C
C. Solid Phase: K ₂ SiO ₃							
M	(61.1)	—	(38.9)	976	—	—	—
51	50.6	8.7	40.7	902	+3-3	0.5	CG
52	47.3	12.1	40.6	833	+4-4	1	CG
53	41.7	11.1	47.2	702	+2-2	2	CG
D. Solid Phase: K ₂ Si ₂ O ₅							
251	43.8	—	56.2	1036	+1-1	1	CG
61	42.3	1.4	56.3	1008	+1-2	1	CG
62	38.4	4.5	57.2	954	+2-3	2	CG
63	36.8	5.5	57.7	924	+2-2	2	CG
64	34.6	7.6	57.8	898	+2-2	2	CG
65	32.9	8.6	58.5	878	+2-2	3	CG
66	30.2	10.9	58.9	831	+1-1	3	C
67	27.0	13.2	59.8	765	+1-1	12	C
68	40.9	1.3	57.8	1000	+1-1	1	CG
69	38.9	1.3	59.8	978	+1-2	1	CG
70	36.9	1.2	61.9	973	+2-2	2	CG
71	35.8	1.2	63.0	951	+2-2	2	CG
72	34.6	1.2	64.2	925	+2-3	2	CG
73	33.9	1.1	65.0	890	+2-2	2	CG
74	32.8	1.1	66.1	861	+3-3	3	C
75	31.9	1.1	67.0	826	+3-3	3	C
76	35.6	4.2	60.2	928	+2-2	3	CG
77	33.6	4.0	62.4	883	+2-3	8	C
78	29.9	3.6	66.4	798	+2-2	12	C
79	31.2	8.0	60.8	860	+5-5	6	C
80	28.9	7.5	63.6	807	+4-4	4	C
81	27.3	7.1	65.6	750	+5-5	6	B

* The symbols G, C, B denote that the material used for the quenching experiments was G glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE I (Continued)
Compositions and Liquidus Temperatures of Preparations studied
Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K ₂ O	Na ₂ O	SiO ₂				
82	25.7	6.6	67.7	667	+2-2	24	B
83	24.7	11.7	63.6	698	+4-4	6	B
84	44.8	1.5	53.7	1002	+2-2	1	CG
85	47.3	1.5	51.2	975	+2-2	1	CG
86	48.4	1.6	50.0	935	+2-3	1	CG
87	49.8	1.6	48.6	865	+5-5	1	CG
88	50.7	1.7	47.6	816	+4-4	1	CG
89	51.6	1.7	46.7	789	+4-4	1	CG
90	46.9	3.7	49.4	860	+5-5	1	CG
91	40.9	4.9	54.2	948	+3-3	1	CG
92	45.0	5.3	49.7	843	+3-3	1	CG
93	35.6	9.3	55.1	864	+4-4	1	CG
94	39.2	10.0	50.8	785	+5-5	1	CG
95	40.5	10.8	48.8	693	+3-3	1	CG
96	34.7	13.1	52.2	730	+5-5	1	CG
97	31.9	15.5	52.5	715	+5-5	1	CG
E. Solid Phase: $K_2Si_4O_9$							
284	28.1	—	71.9	765	+0.5-0.5	24	B
101	26.9	3.2	69.9	700	+2-2	24	B
F. Solid Phase: Quartz							
110	24.5	2.9	72.6	798	+4-4	48	B
111	23.4	6.0	70.6	700	+10-10	75	B
112	20.9	5.5	73.6	810	+5-5	24	B
113	16.0	11.3	72.7	783	+4-4	24	B
114	13.3	15.7	71.0	688	+4-4	50	B
115	9.1	18.9	72.0	750	+5-5	24	B
116	8.2	16.9	75.0	865	+5-5	30	B
117	5.3	21.7	73.0	786	+3-3	30	B
G. Solid Phase: Tridymite							
121	22.4	2.6	75.0	902	+3-3	6	C
122	20.9	2.6	76.5	976	+4-4	4	C
123	16.9	2.8	80.3	1168	+4-4	2	C
124	17.9	4.6	77.5	1035	+5-5	4	C
125	14.3	10.2	75.5	905	+5-5	5	C
126	10.5	7.4	82.1	1235	+5-5	3	C
127	7.2	15.4	77.4	980	+5-5	5	C
128	4.0	11.7	84.3	1310	+5-5	3	C

* The symbols G, C, B denote that the material used for the quenching experiments was glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE II
Invariant Points*

Type	Crystal phases in coexistence with liquid	t°C	Composition of liquid weight per cent		
			K ₂ O	Na ₂ O	SiO ₂
E ₁	Ternary eutectic				
E ₂	"	645	40.1	11.7	48.2
E ₃	"	665	25.4	17.2	57.4
E ₄	Binary eutectic	540	23	8	69
E ₅	"	775	54.5	—	45.5
E ₆	"	752	31.0	—	69.0
E ₇	"	764	27.6	—	72.4
E ₈	"	846	—	37.9	62.1
E ₉	"	793	—	26.1	73.9
E ₁₀	"	745	43	15	42
A	Unmixing	705	24.5	15.0	60.5
B	"	814	52.5	—	47.5
C	"	993	40.4	—	59.6
D	"	740	11.5	27.0	61.5
F	Inversion	765	4.0	23.5	72.5
G	"	678	25.0	16.3	58.7
H	"	678	22.0	19.5	58.5
J	"	678	23.6	13.7	62.7
		678	14.4	15.4	70.2

*For a crystallographic description of the compounds see Refs. 1, 2, and 3.

TABLE II (Continued)
Invariant Points*

Type	Crystal phases in coexistence with liquid	t°C	Composition of liquid weight per cent		
			K ₂ O	Na ₂ O	SiO ₂
K	Inversion				
L	"	596	22.9	9.3	67.8
M	"	596	24.6	5.7	69.7
N	"	573	23.8	6.5	69.7
O	"	573	20.6	9.8	69.6
P	Reaction	640	25.7	4.5	69.8
Q	Inversion	870	25.6	—	74.4
R	"	870	—	24.5	75.5
S	"	1470	10.5	—	89.5
T	"	1470	—	11.3	88.7
U	Eutectic	680	28.7	17.6	53.7
V	Unmixing	923	36.8	5.5	57.7
—	"	742	10.3	26.0	63.7
—	Melting	976	61	—	39
—	"	1089	—	50.8	49.2
—	"	1036	43.95	—	56.05
—	"	875	—	34.04	65.96
—	"	765	28.16	—	71.84
—	"	1713	—	—	100
—	Cristobalite				

* For a crystallographic description of the compounds see Refs. 1, 2, and 3.

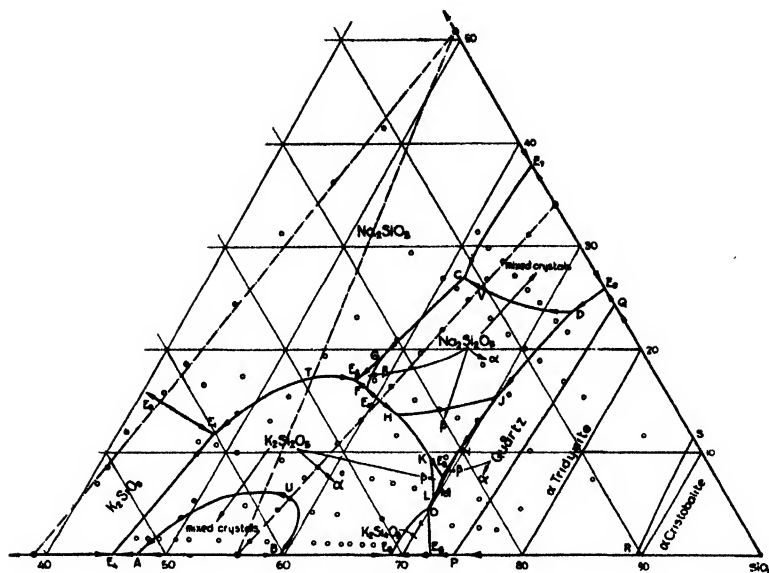


FIG. 1

The ternary system, K_2SiO_3 - Na_2SiO_3 - SiO_2 . This figure shows the compositions of the mixtures studied represented by open circles; the compositions of the binary potassium and sodium silicates by black circles, and the fields of the compounds.

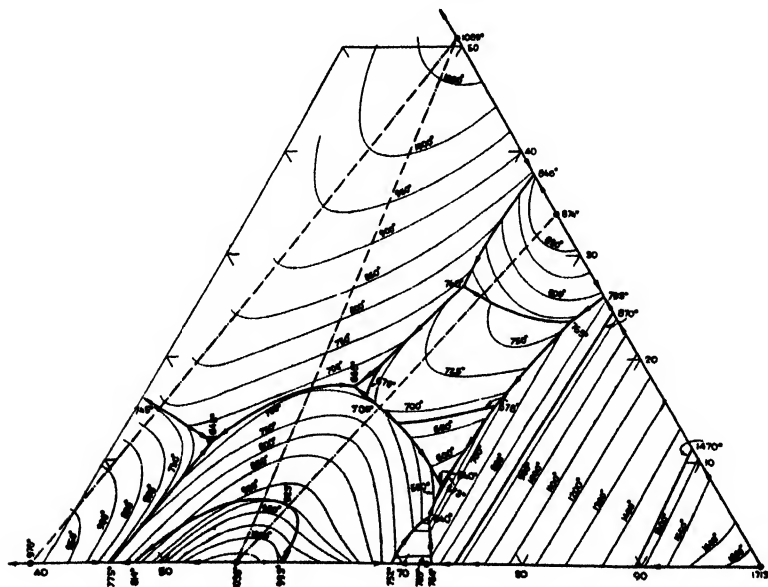


FIG. 2

The ternary system, K_2SiO_3 - Na_2SiO_3 - SiO_2 . This diagram shows the isotherms of the liquidus surfaces of the various compounds.

Discussion of the Ternary System

The equilibrium diagrams of Figs. 1 and 2 present the stability fields of the crystalline compounds occurring in the system. It will be seen by reference to the figures that there are no ternary compounds and no incongruent melting relations between the adjacent binary compounds, hence the system is one of comparative simplicity. The only complications entering are due to the unique type of solid solution relations of the disilicates, and the polymorphic relations of the compounds, $Na_2Si_2O_6$, $K_2Si_2O_6$, and the various modifications of silica, namely, high and low quartz (Quartz I and II), tridymite, and cristobalite.

In addition to the component binary systems along the binary boundaries there are three binary systems within the ternary system, K_2SiO_3 - Na_2SiO_3 - SiO_2 , namely, K_2SiO_3 - Na_2SiO_3 , $K_2Si_2O_6$ - $Na_2Si_2O_6$, and $K_2Si_2O_6$ - Na_2SiO_3 . Two other possible binary systems, K_2SiO_3 - $Na_2Si_2O_6$ and $K_2Si_4O_9$ - $Na_2Si_2O_6$, fail to appear. The first of these is excluded by the existence of the binary system, $K_2Si_2O_6$ - Na_2SiO_3 , the second fails to be realized at the liquidus as a consequence of the excessive area covered by the liquidus surface of $K_2Si_2O_6$.

The melting relations for the ternary system accordingly are composed of the liquidus surfaces of K_2SiO_3 , Na_2SiO_3 , $K_2Si_2O_6$, $Na_2Si_2O_6$, $K_2Si_4O_9$, quartz, tridymite, and cristobalite. The ternary system may be thought of in terms of three subsidiary ternary systems: (1) K_2SiO_3 - Na_2SiO_3 - $K_2Si_2O_6$, with a ternary eutectic at 40.1 wt. per cent K_2O , 11.7 wt. per cent Na_2O and 48.2 wt. per cent SiO_2 , 645°C; (2) $K_2Si_2O_6$ - Na_2SiO_3 - $Na_2Si_2O_6$, with a ternary eutectic at 25.4 wt. per cent K_2O , 17.2 wt. per cent Na_2O , and 57.4 wt. per cent SiO_2 , 665°C; (3) $K_2Si_2O_6$ - $Na_2Si_2O_6$ - SiO_2 (Quartz II), with a ternary eutectic at 22.9 wt. per cent K_2O , 7.6 wt. per cent Na_2O and 69.5 wt. per cent SiO_2 , 540°C. A list of the various invariant points encountered in the system is given in Table II; Figs. 3 and 4 represent the binary systems, K_2SiO_3 - Na_2SiO_3 and $K_2Si_2O_6$ - $Na_2Si_2O_6$. The binary system, $K_2Si_2O_6$ - Na_2SiO_3 , was not separately investigated, and hence is not represented.

The liquidus surfaces of K_2SiO_3 and Na_2SiO_3 are simple curved sheets and need no further discussion.

The liquidus surfaces of the different varieties of silica rise steeply in succession from the ternary eutectic for $K_2Si_2O_6$, $Na_2Si_2O_6$, and quartz II at 540°, with inversion boundaries 573° for quartz II and quartz I, 870° for quartz I and tridymite, 1470° for tridymite and cristobalite. The stability relations for the different varieties of silica are those determined by Fenner.⁹ The liquidus surface for cristobalite necessarily exhibits a fold in consequence of the difference in the liquidus curves for cristobalite in the component-binary systems, K_2O - SiO_2 and Na_2O - SiO_2 , the curve in the latter system exhibiting a reverse S curvature. The liquidus surfaces of tridymite, quartz I and quartz II are smooth sheets with no special features. The low ternary eutectic temperature for $K_2Si_2O_6$ II, $Na_2Si_2O_6$ II, and quartz II is noteworthy. This was investigated by the method employed by Morey and Bowen in their study of the system, Na_2SiO_3 - $CaSiO_3$ - SiO_2 .¹⁰ Crystallized

⁹ C. N. Fenner: *Am. J. Sci.*, **36**, 331 (1913).

¹⁰ Morey and Bowen: *J. Soc. Glass Tech.*, **9**, 226 (1925).

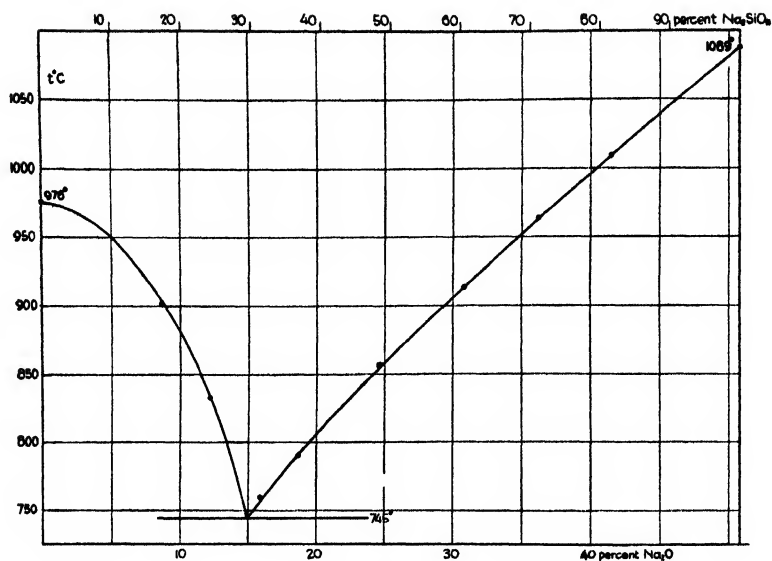


FIG. 3

Section through ternary diagram, showing the binary system, $\text{K}_2\text{SiO}_3\text{-Na}_2\text{SiO}_3$.

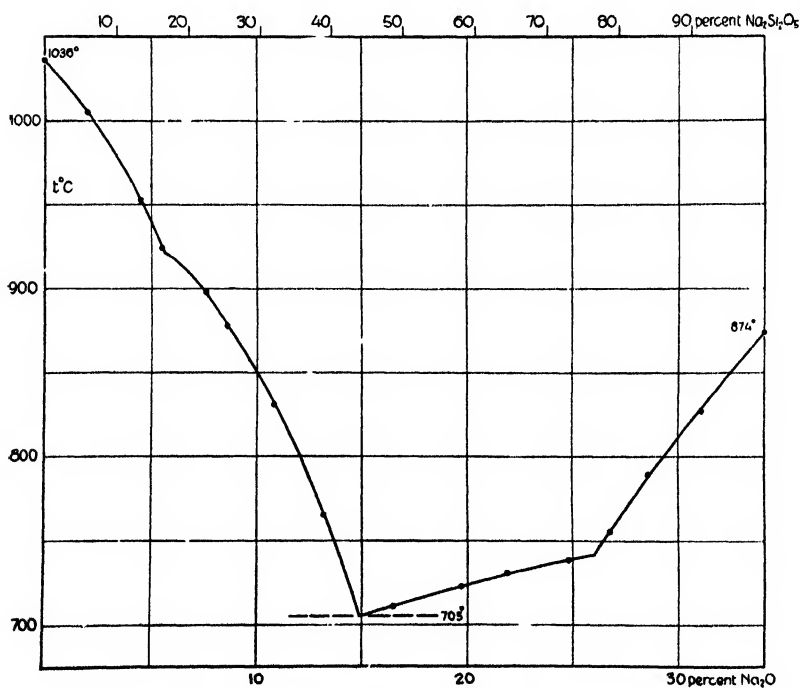


FIG. 4

Section through ternary diagram, showing the binary system, $\text{K}_2\text{Si}_2\text{O}_5\text{-Na}_2\text{Si}_2\text{O}_5$.

$Na_2Si_2O_5$, $K_2Si_2O_5$, and extremely finely powdered quartz were ground together in the required proportions and samples of the mixtures were held at various constant temperatures to determine the point at which sintering and glass formation take place. The most probable value thus determined is 540°C ; the uncertainty is about $\pm 30^\circ\text{C}$. The reactions between silicates at such low temperatures are extremely slow, and even 5 to 10 days heating at a given temperature above the eutectic does not serve to completely dissolve quartz crystals.

The field of $K_2Si_4O_9$ occupies only a small portion of the ternary diagram. This compound exists in two polymorphic modifications with an inversion at 592° at the pressure of 1 atmosphere.¹¹ The lowest liquidus temperature with $K_2Si_4O_9$ as the stable phase in the ternary system is 640° for the equilibrium between $K_2Si_4O_9$ I, $K_2Si_2O_5$ I, quartz I and liquid, and hence the low temperature modification, $K_2Si_4O_9$ II does not reach the liquidus.

The disilicates, $K_2Si_2O_5$ and $Na_2Si_2O_5$, present interesting features. Reference to Fig. 4 shows that the liquidus curves of both these compounds in their binary system exhibit breaks, at 920° for $K_2Si_2O_5$, and at 742° for $Na_2Si_2O_5$. Reference to the work on the binary systems, K_2SiO_3 - SiO_2 and Na_2O - SiO_2 ,^{1,2} reveals that in the potash system corresponding breaks are encountered at 814° on the K_2O side, and at 993° on the SiO_2 side of the $K_2Si_2O_5$ composition. In the soda system heat effects were located at 706° on the Na_2O side, and at 768° on the SiO_2 side of the $Na_2Si_2O_5$ composition, below the liquidus temperatures throughout. The interpretation was that both $K_2Si_2O_5$ and $Na_2Si_2O_5$ enter into solid solutions with excess SiO_2 , and excess K_2O and Na_2O respectively, the different temperatures established being the unmixing temperatures of these solid solutions. Below the unmixing temperatures the crystals are essentially the pure disilicates, as evidenced by the constancy of inversion temperatures, 596°C for $K_2Si_2O_5$ I and $K_2Si_2O_5$ II, and 678° for $Na_2Si_2O_5$ I and $Na_2Si_2O_5$ II.

In the ternary system a search was made for the existence of possible compounds which might explain the presence of the above-mentioned breaks at 920° and 742° in the subsidiary binary system, $K_2Si_2O_5$ - $Na_2Si_2O_5$. This search revealed that no such compounds exist, but that the unmixing boundaries AB and CD (Fig. 1) are not constant temperature lines; they are screw curves, the temperature rising continuously from A, 814°C to B at 992°C , the intersection of the screw curve with the disilicate join being at 920° at U, for the $K_2Si_2O_5$; in the case of the $Na_2Si_2O_5$ the screw curve is entirely within the ternary system, rising from C at 740° through V at 742° to D at 765° , the two ends of the screw curve being at 706° and 768° respectively, under the liquidus surface. The unmixing and the polymorphic inversions in these two compounds are prompt, hence no definite optical evidence for the existence of the solid solutions is adducible. In the case of the $Na_2Si_2O_5$ a slight modification of the external form of the crystals was noticed, but this was not sufficient for a description. The relations may then be summarized in the statement that both $Na_2Si_2O_5$ and $K_2Si_2O_5$ take up limited excess of SiO_2 ,

¹¹ Goranson and Kracek: J. Phys. Chem., **36**, 913 (1932).

Na_2O , or K_2O , respectively, depending on the composition of the liquid from which they crystallize, in the component-binary systems, and that $\text{K}_2\text{Si}_2\text{O}_5$ takes in a limited amount of Na_2O , while $\text{Na}_2\text{Si}_2\text{O}_5$ takes in a limited amount of K_2O in the ternary system under description.

In addition to the above-described solid solution phenomena, the liquidus surfaces of $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{Na}_2\text{Si}_2\text{O}_5$ show the inversion temperatures $\text{K}_2\text{Si}_2\text{O}_5$ I to $\text{K}_2\text{Si}_2\text{O}_5$ II at 596° and $\text{Na}_2\text{Si}_2\text{O}_5$ I to $\text{Na}_2\text{Si}_2\text{O}_5$ II at 678° .

The temperatures of the eutectics E_1 and E_2 , namely $\text{K}_2\text{SiO}_3 + \text{K}_2\text{Si}_2\text{O}_5$ I + $\text{Na}_2\text{SiO}_3 + \text{L}$ and $\text{K}_2\text{Si}_2\text{O}_5$ I + $\text{Na}_2\text{SiO}_3 + \text{Na}_2\text{Si}_2\text{O}_5$ II + L , were determined by quenching previously crystallized preparations heated at the various appropriate constant temperatures and examining with the microscope for the first appearance of glass. The compositions employed for this purpose were Nos. 53 and 95 for E_1 and 12 for E_2 . The compositions used do not melt completely at the eutectic temperatures. These eutectic temperatures were located with an uncertainty of $\pm 10^\circ$, the uncertainty being due to the difficulty of recognizing the first traces of glass in the microscopic examination.

From the physical-chemical point of view it is of interest to note that the liquidus surfaces of the silicate compounds of the system are sheets with very flat maxima at the melting points, and generally with a large radius of curvature. This indicates considerable dissociation of these silicates in the liquid state.¹² The extensive dissociation of the liquid is also indicated by the relatively low melting points, with the statistical implication that the silicates are not definite compounds in the melts, particularly at higher temperatures. The situation is, in a sense, analogous to that encountered with other additive compounds; for example, while $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ undoubtedly is present in CaCl_2 - H_2O solutions in appreciable amounts at the melting point of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, it is probable from the point of view of statistical mechanics that the number of molecules of H_2O associated with one of CaCl_2 (or Ca^{++}) in solution depends upon average distribution governed by the intermolecular forces in the liquid, rather than upon the definite distribution governed by the directional forces in the lattice of a crystal.

Summary

The melting point relations in the ternary system, K_2SiO_3 - Na_2SiO_3 - SiO_2 , are simply-eutectoid with respect to the component-binary systems, K_2SiO_3 - SiO_2 and Na_2SiO_3 - SiO_2 , there being no ternary compounds. A unique type of solid solution formation is encountered in the disilicate region, both $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{Na}_2\text{Si}_2\text{O}_5$ taking up a varying limited excess of the three constituents, K_2O , Na_2O , SiO_2 , dependent upon the composition of the liquid in equilibrium with the crystals. The equilibrium diagrams of Figs. 1 and 2 present the phase relations worked out by the method of quenching, the data being given in Tables I and II.

*Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1932.*

¹² W. Stortenbeker (upon suggestions of H. A. Lorentz): *Z. physik. Chem.*, **10**, 183, 194 (1892), discussed by Lewis and Randall: "Thermodynamics," 217 (1923); see also A. Smits: *Z. physik. Chem.*, **78**, 708 (1912); Morey and Bowen: *Ref. 3*; J. W. Gibbs: "Scientific Papers," **1**, 135.

THE EFFECT OF X-RADIATION ON THE VISCOSITY OF GELATINE*

BY HELEN QUINCY WOODARD

Introduction

The effect of various types of radiation on a number of organic and inorganic colloids has been reported in the literature. Fernau,¹ Fernau and Pauli,² Crowther and Fairbrother,⁴ Fairbrother,³ and Crowther⁵ have made a thorough study of the effect of different types of radiation on ceric hydroxide sols and other inorganic colloids. They found in general that positive sols could be coagulated or rendered less stable by β , γ or X-rays, while negative sols were relatively unaffected. The doses required to produce measurable effects were large. There is a difference of opinion among these authors as to the role of H_2O_2 as an intermediate in the process of coagulation.

In the study of the effect of radiation on organic colloids Fernau and Pauli² found that albumins were flocculated by β and γ radiation. Fairbrother⁶ found that the viscosity of egg albumin was decreased permanently by large doses of X-rays, and Fernau and Pauli⁷ found that β and γ radiation decreased the viscosity of gelatine. Fernau⁸ found that the coagulation temperature of serum and egg albumin was lowered by radium radiation. Wels and Thiele⁹ gave sub-therapeutic X-ray doses to globulin sols, and found that the radiation caused aggregation of the particles. Loiseleur¹⁰ found that the radiation from radium caused the flocculation of gelatine.

A good deal of other work has been done on the effect of various types of radiation on different colloids, but, because of the complexity of the systems used or the unsatisfactory character of the methods of observation, the results admit of no definite interpretation. Even among the most clear-cut results, as those reviewed above, there is much conflict.

In the present work the effect of moderately hard X-rays on the viscosity of dilute gelatine solutions was studied. Gelatine was chosen for the investigation because it is an organic colloid the properties of which are well known from the work of Loeb and Wilson. Viscosity was chosen as the property to be observed in the hope that observations on viscosity change might throw some light on the effect of X-rays on living tissues. This seemed possible, since the swelling of tissues which have been exposed to X-rays may be due to a change in the viscosity of the cell contents.

Apparatus and Materials

The gelatine used was "Coignet" gelatine from Akatos, Inc., New York City. It was obtained in thick sheets, and gave a pH of about 5.2 when dissolved in water. The water used for preparing the sols was redistilled from

* From the Huntington Fund for Cancer Research, Memorial Hospital, New York City.

KMnO₄ solution. Chemicals of "C.P." and "T.P." grade from Eimer and Amend were used throughout. The pH of the sols was determined colorimetrically to 0.1 pH by comparison with buffer standards from the LaMott Chemical Supply Co.

The sols were prepared by placing a weighed piece of dry gelatine in a flask, adding the required amount of water, HCl, or NaOH, placing the flask in a boiling water bath for exactly 5 min., removing the flask, shaking until the gelatine was dissolved, and then cooling with running cold water. The maximum temperature reached by the sol during 5 min. in the water bath was about 85°C. The time of shaking required to dissolve the gelatine was from ten to twenty minutes, and this difference in the time during which the sols were held at a high temperature accounted for considerable differences in the viscosity.

The sols were irradiated in crystallizing dishes 46-49 mm. in diameter covered by watch glasses 1.0-1.8 mm. thick. Thirty cc. samples were used. Sols irradiated in dishes with this range of diameters showed radiation effects identical within the experimental error. The X-ray setting was 200 K.V., 30 m.a., distance target to bottom of dish 42 cm., no filter, 40 min. exposure. The X-ray tube was of the new thick-walled type. The glass was about 5 mm. thick, and this was sufficient to filter out the softest radiation. The machine delivered about 270 roentgens per minute at this setting, so that the total dose amounted to about 10800 roentgens.

Viscosities were determined in an Ostwald viscometer immersed in a water bath with a temperature range of 24.7°-25.3°C. The viscometer was calibrated for 5 cc. of water for every tenth of a degree from 24.° to 26.° C. The temperature was noted for every viscosity reading on gelatine, and the relative viscosity of the gelatine was calculated as, relative viscosity = R.V. = time of delivery for gelatine at t° divided by time of delivery for water at t° . The water value of the viscometer at 25°C. was 78.3 sec. and successive values checked to ± 0.1 sec. The water value was determined at least once a day. When the viscosity of a large number of gelatine sols was determined on the same day, the viscometer was cleaned with sulfuric and chromic acids and the water value checked after every eight determinations.

Successive readings on the same sample of gelatine gave readings identical to ± 0.1 sec. with no drift that would suggest a structural viscosity. Tests were made with different volumes of sol, 3.0, 5.0, and 7.5 cc. These differences in volume caused the sols to flow under different pressures. The value for R.V. was found to change with pressure, and this showed that the viscosity was in fact structural. These tests were made on gelatine sols of pH 3.3-3.5 over a concentration range of 0.2%-1.0%.

Experimental

Preliminary work showed that the viscosity of gelatine sols was decreased by irradiation, and that the difference between irradiated and control sols was greater the greater the initial viscosity of the sol. The viscosity of a gelatine

sol of given concentration may be changed by heat, by age, by the addition of salts, by change in pH and by irradiation. These viscosity changes are brought about by different changes in the structure of the colloid.

The effect of ageing at moderate temperatures (37°C. and below) is apparently the slow establishment of a reversible equilibrium between α and β gelatine, which possess different colloidal properties. The effect of more severe heating is an irreversible disaggregation of the gelatine micelles, with great decrease in viscosity, but without change in chemical properties unless the heating is very prolonged.¹⁴ The two types of change are probably closely connected. The addition of salts lowers the viscosity by changing the degree of swelling of the colloidal micelles through the well-known Donnan equilibrium effect. Change in pH also alters the viscosity through change in the Donnan equilibrium, and, in addition, changes the degree of ionization of the gelatine. The nature of the change brought about by irradiation is unknown.

A study was made of the differences in the effect of radiation on gelatine sols the viscosity of which had been changed in these five ways. In addition, differences in the effect of radiation on sols of different concentration were studied.

As it was not possible to make up successive sols of the same concentration and pH value which had the same viscosity, such sols could not in general be plotted on the same curve. In order to obtain a direct comparison between two or more sols it was necessary to take the initial relative viscosity of the control samples as 100%. Subsequent values of the control and experimental samples were then calculated as percent of this initial value. In this way figures for successive experiments could be compared directly, provided the initial viscosities did not differ too greatly. Sols of very different initial viscosities could not be compared by this method, however, since the percentage change in viscosity produced by a given quantity of radiation was greater the more viscous the sol.

In most of the work it was necessary to compare sols of different initial viscosities. In this work the viscosity of the control samples, $R.V._c$, was plotted directly against the percent reduction of viscosity produced by radiation,

$\frac{R.V._c - R.V._e}{R.V._c}$. In each of these experiments different portions of the

same sols were treated in different ways and irradiated at the same time. Where a series of such sols is plotted on the same figure, the points representing percent reduction in viscosity of the untreated portion of each sol are plotted thus (x); points representing percent reduction of viscosity of the treated portions of the sol are represented thus (.). The degree of scattering of the points representing untreated sols is a measure of the experimental error and of the variations in the material used. Where the width of the band defined by points for the treated sols is not greater than that of the portion of the band defined by the points for the initial sols, it is considered that the effects observed are produced by the treatment and are not the result of experimental error.

Since differences in the temperature at which gelatine sols are kept produce permanent changes in viscosity, all sols were kept at the same temperature (25°C.) except while the experimental sols were being irradiated. During this period the control sols were kept at room temperature. The difference between the temperatures of liquids in the X-ray chamber and in the room outside the chamber did not exceed 3°C. In order to determine whether either this slight change in temperature or the ozone and oxides of nitrogen produced by the X-rays would affect the viscosity of gelatine, sols were placed in a part

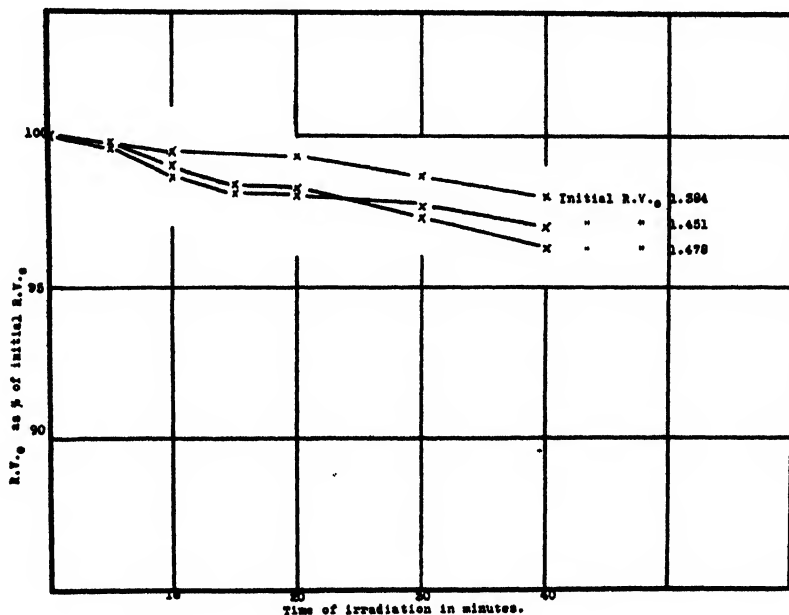


FIG. 1

Change of Viscosity with Time of Irradiation

of the chamber which was shielded from radiation, and the machine was operated for 40 minutes. No significant difference was observed between sols so treated and sols kept at room temperature. A further test of the temperature effect was made by placing a portion of a sol in the 37°C. incubator for one hour and then returning it to the 25°C. incubator where the control was kept. A small reduction in the relative viscosity (0.7%) was observed, which persisted for 48 hours. As the temperature difference used here was four times as large as that which was found following irradiation, and as the viscosity change was much smaller than most of the changes observed after irradiation, it is felt that temperature changes in the gelatine sols in the X-ray chamber produced no significant differences in the results.

The effect of different doses of radiation delivered to portions of the same sol within a one hour period is shown in Fig. 1. The radiation effect increases fairly regularly with time of irradiation but is not directly proportional to time. The figure also illustrates the difference in the radiosensitivity of sols

with different initial viscosities. The two sols for which the relative viscosity of the controls 24 hours after irradiation were 1.451 and 1.477 showed a reduction of these viscosities of 3.0% and 2.7% respectively, while the sol for which the relative viscosity of the control was only 1.384 has this value reduced by only 2%.

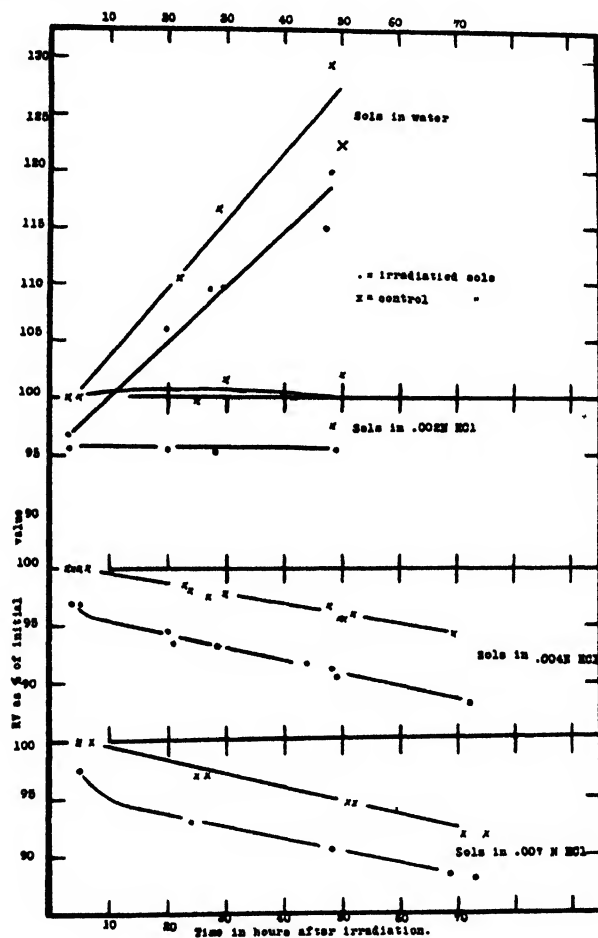


FIG. 2
Change of Viscosity with Time

The change in the radiation effect with time after irradiation is shown in Fig. 2. This shows the relative viscosities of irradiated and control sols containing 0.4% gelatine dissolved in water and in 0.002 N HCl, 0.004 N HCl, and 0.007 N HCl at different times after irradiation, all values being calculated as percent of the values for the controls on the day of irradiation. It is seen that the difference between irradiated and control sols is approximately constant after 24 hours. The viscosity of both irradiated and control sols of pH greater than 3.8 rises with time; that of sols with a lower pH falls with time. The

curves for sols in 0.001 N HCl, 0.003 N HCl, 0.005 N HCl, and 0.006 N HCl occupy positions intermediate with those shown in the figure, while those for sols in 0.008 N HCl, 0.009 N HCl and 0.010 N HCl are similar to those for sols in 0.007 N HCl.

In the subsequent work the radiation effects reported are values for irradiated and control sols read 20-30 hours after irradiation. It is felt to be more satisfactory to compare the values for R.V.₀ and R.V._∞ at the same time, rather than to compare the values for R.V.₀ with the R.V. of the controls at the time of irradiation, since the former method is not confused by the changes which both irradiated and control sols undergo with time. Unless otherwise stated, all the irradiated sols in the subsequent work were irradiated for 40 minutes.

Effect of Heat

Fig. 3 shows the effect of heat on the radiosensitivity of 0.4% gelatine sols in 0.004 N HCl, pH 3.3. The initial sols were made up in the usual way by heating for 5 min. on the water bath and shaking until the gelatine was all dispersed. Samples were then withdrawn while the sol was still hot and cooled immediately, the remainder being put back in the water bath for different periods up to 90 min. The initial sols reached a temperature of 86° in 5 min. The maximum temperature observed in subsequent heatings was 94°. Half of each sample was then irradiated and the remainder kept as a control. The wide range of the abscissas in the figure shows that the relative viscosities of the controls were greatly reduced by heat.

In the figure the percent reduction of the relative viscosity of each irradiated sample $\frac{RV_c - R.V._\infty}{R.V._\infty}$ is plotted against the relative viscosity of its control, R.V._∞. It is seen that the radiation effect decreases with decreasing relative viscosity of the controls and reaches zero for a sol for which R.V._∞ = 1.073. Initial sols are marked (x); sols heated for longer periods than 5 min. are marked (.). The variation of the heated sols is not greater than that of the controls.

It is probable that gelatine when heated for 90 min. at 90°C. is almost entirely converted into the β form. Since these heated sols were not radiosensitive, it appears that under the conditions employed in the present work, it is only the α form which is sensitive to X-rays.

Effect of Added Salts

Fig. 4 shows the effect of added salts on the viscosity and radiosensitivity of 0.4% gelatine in 0.004 N HCl. Eight-tenths percent sols in 0.008 N HCl were made up and then diluted to 0.4% with solutions of different salts so that the final salt concentration was 0.004 N. The salts were used NaCl, KCl, Na₂SO₄, HgCl₂, KH₂PO₄, K₂CrO₄, NaNO₂, NaNO₃, NH₄Cl, (NH₄)₂SO₄. Sols without added salts are plotted thus (x); sols with added salts are plotted thus (.). The relative viscosity of the controls was reduced by the addition of salts in the manner to be expected from the Donnan equilibrium relations.

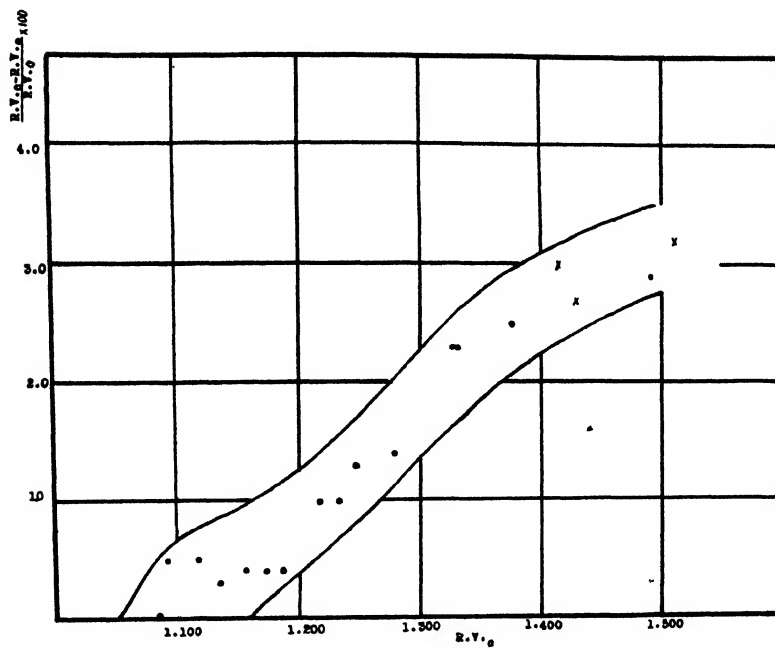


FIG. 3
Effect of Heat on Radiosensitivity

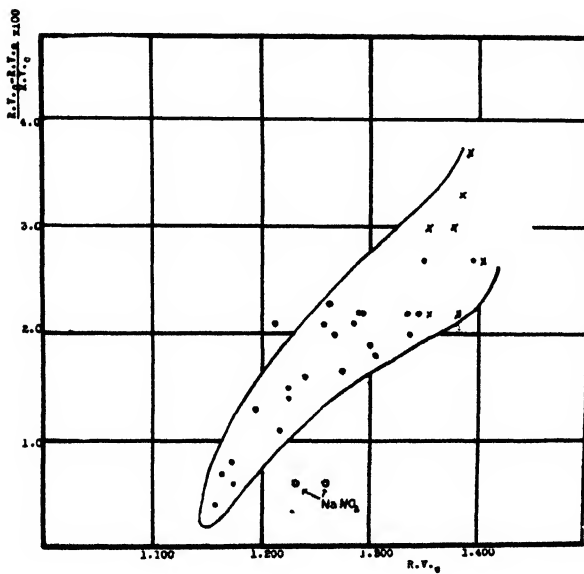


FIG. 4
Effect of added Salts on Radiosensitivity

It is seen that, when the relative viscosity of the gelatine is decreased by the addition of salts the radiosensitivity is also decreased. With the exception of sols to which NaNO_2 has been added, the variation of the treated sols is not greater than that of the controls. The disproportionately great reduction in radiosensitivity brought about by NaNO_2 is probably due to the fact that nitrous acid, which is liberated from the nitrite in acid solution, reacts chemically with the gelatine. The effect of this salt is therefore more than a simple change in Donnan equilibrium.

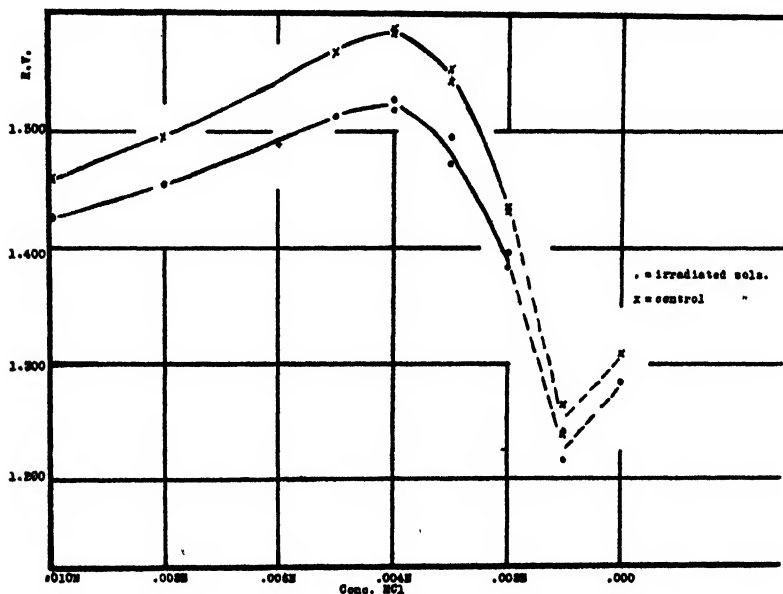


FIG. 5
Effect of pH on Viscosity and Radiosensitivity

The addition of none of these salts altered the pH of the sols more than 0.2 pH. Slight changes in pH in the neighborhood of pH 3.3 do not alter the radiosensitivity, as is shown in the subsequent section.

Effect of pH

Eight-tenths percent gelatine sols were made up in water. Several portions of each sol were then diluted to 0.4% with HCl of different concentrations. Half of each sample was then irradiated, the remainder being kept as a control. Two of these sols were so nearly of the same initial concentration that they could be plotted directly on the same curve. Fig. 5 shows the relative viscosities of irradiated and control samples of these sols plotted against concentration of HCl. It is seen that, in general, the radiation effect as shown by the distance between the two curves is greater for the more viscous sols. A sol of given viscosity on the acid side of pH 3.3 is less sensitive than one on the alkaline side however. In Fig. 6, the relative viscosity of the controls is

plotted against the percent reduction of relative viscosity of the experimental sols for sols of pH 3.3 or less. It is seen that the radiosensitivity decreases with decreasing relative viscosity. The same effect was observed for sols of pH greater than 3.3, but the experimental error was too large for definite conclusions. The difference in the behavior of sols on the acid and alkaline sides of the point of maximum viscosity shows that some other factor than viscosity affects the radiosensitivity.

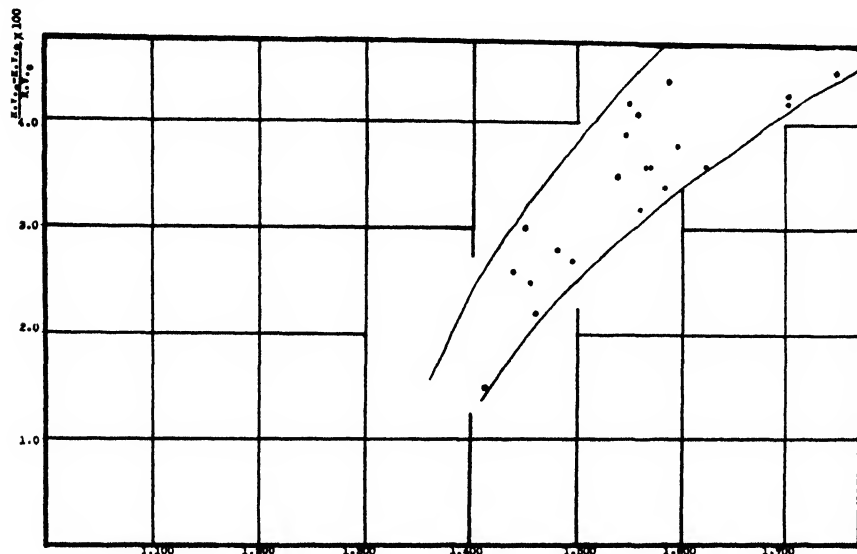


FIG. 6
Effect of pH on Radiosensitivity

Effect of Time

The relative viscosity of 0.4% gelatine of pH 3.3 decreases with time as was shown above; that of 0.4% gelatine of pH 5.6 increases with time. If it is true in general that radiosensitivity is a function of viscosity, then we should expect the radiosensitivity of gelatine of pH 3.3 to decrease with time and that of gelatine of pH 5.6 to increase with time. It was found that the radiosensitivity of gelatine of pH 3.3 does in general decrease with time, although the experimental error is too large for satisfactory quantitative work. No quantitative work was possible with sols of pH 5.6, as these nearly isoelectric sols are extremely variable.

Effect of Previous Irradiation

Since the viscosity of gelatine is reduced by radiation, it is interesting to determine whether this reduction in viscosity is accompanied by a reduction of sensitivity to further irradiation. The experiment is complicated by the fact that the radiation effect increases for at least 24 hours after exposure. Hence it is necessary to irradiate different portions of a sol at 24 hour intervals.

The radiosensitivity of each portion is then determined by comparing its viscosity 24 hours after the last irradiation with that of the sample which has received one less exposure. This prolongs the experiment and so increases the experimental error that the results are not clear cut. In general, however, it is found that, when the viscosity is reduced by irradiation, the sensitivity to further irradiation is also reduced.

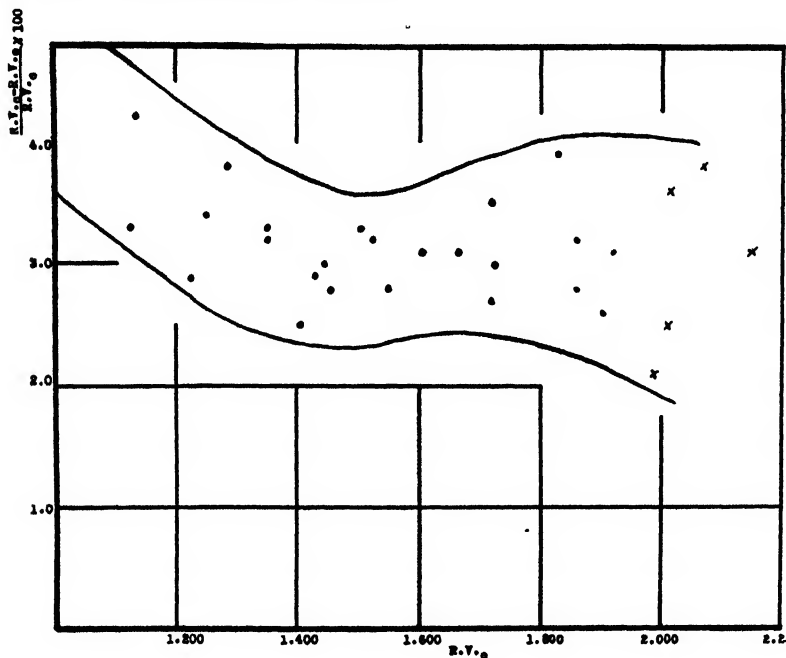


FIG. 7
Effect of Concentration on Radiosensitivity

Effect of Concentration

The methods previously described of changing the viscosity of 0.4% gelatine sols have changed the colloidal state of a given quantity of gelatine. A series of dilutions of the same sol differ in the closeness of packing of the micelles, but probably do not differ in the colloidal structure of the micelles, unless the concentration of some of the dilutions is sufficiently great for incipient gelation. In order to study the effect of radiation on sols of different viscosity but of the same structure, the radiosensitivity of a series of dilutions of the same sol was determined. One percent sols were made up in 0.010 N HCl, and a series of dilutions was made from each sol, so that the final concentrations ranged from 0.1% to 1.0%. The pH range of these dilutions was 3.3 to 3.5. It was shown in a previous section that sols of the same concentration have approximately the same sensitivity over this range. Half of each sample was then irradiated. The results are shown in Fig. 7. The initial sols are represented thus (x); the diluted sols are represented thus (.). The variation between the diluted sols is less than that between the initial sols. This series

is entirely different from the preceding ones in that the more dilute and less viscous sols show a percent reduction in viscosity following irradiation as great as, or greater than, the percent reduction in the viscosity of the more concentrated sols.

Discussion

It appears from this work that X-rays reduce the viscosity of gelatine by reducing the swelling of the colloidal micelles. The more swollen are the micelles at the time of irradiation, the greater is the reduction in swelling brought about by the irradiation. When the degree of swelling of the micelles is reduced before irradiation, then the further reduction brought about by irradiation is slight. This is true whether the reduction in swelling is brought about by a shift of the gelatine from the α to the β form, by a change in the Donnan equilibrium conditions, or, qualitatively at least, by the effect of radiation itself. Further confirmation of the theory that the effect of radiation is on the swelling of the micelles is given by the fact that, when a sol is so diluted that the viscosity but not the structure is changed, the percent reduction in viscosity due to irradiation remains the same for different dilutions.

The evidence in the present paper is not sufficient to show that the degree of swelling of the micelles at the time of irradiation is the only property which determines the effect of irradiation. Other factors probably modify the reaction, and, in particular, the effect of X-rays on alkaline sols deserves further study.

Summary

The viscosity of dilute gelatine sols is decreased by heavy doses of X-rays.

When the viscosity of a given gelatine sol is reduced by heat, by pH change, or by the addition of salts, the percent reduction in viscosity due to subsequent irradiation is decreased.

When the viscosity of a given gelatine sol is reduced by ageing or by irradiation, the percent reduction in viscosity due to subsequent irradiation is decreased, but in a manner too irregular for quantitative interpretation.

When the viscosity of a given gelatine sol is reduced by dilution, the percent reduction in viscosity due to subsequent irradiation is not changed.

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DIELECTRIC CONSTANT OF ETHYL ALCOHOL VAPOR AND POSSIBLE EFFECT OF CONDUCTIVITY*

Abstract

The usual heterodyne beat method was used for determining the dielectric constant of ethyl alcohol vapor. Parts of the apparatus are described briefly and the method of calibrating the series condenser is discussed. Dielectric data were taken at a number of different temperatures over complete ranges of pressure. Except in the vicinity of the saturation pressure, $\frac{3(K-1)}{(K+2)}$ was found to vary linearly with p' , the ideal vapor pressure. Near saturation the slopes of the dielectric constant versus pressure curves increased quite markedly. The magnitude of this deviation was found to vary considerably with the solid insulators used in the test condenser. The value of the electric moment as determined from the slopes of the lower parts of the dielectric constant versus pressure curves is $1.68_8 \times 10^{-18}$. This value agrees closely with Miles' value of 1.69₆, and seems definitely to rule out Sanger's value of 1.11.

Complete data were taken of the direct current resistance of the test condenser at the various temperatures and pressures. The resistance was found to decrease rapidly near the saturation vapor pressure. Theoretically, this lowered leakage resistance is shown to be insufficient to account directly for the abnormally high dielectric constant values near saturation.

Introduction

The validity of the Debye equation has been tested for a large number of liquids and gases, and for a few vapors. In particular, measurements on ethyl alcohol vapor have been made by Badeker,¹ Sanger,² and Miles.³ Debye⁴ has also made a calculation of the electric moment of the vapor molecule from refractive index data. Of these, the most recent and reliable data are those obtained by Miles.

Since the number of molecules present per unit volume of the vapor dielectric is proportional to the ideal pressure, Debye's equation in the simplified form may be written⁵

$$3 \frac{K-1}{K+2} \frac{RT^2}{p'} = AT + B$$

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¹ K. Badeker: *Z. physik. Chem.*, **36**, 305 (1901).

² R. Sanger: *Physik. Z.*, **28**, 455 (1927).

³ J. B. Miles: *Phys. Rev.*, (2) **34**, 964 (1929).

⁴ Marx: *Handbuch der Radiologie*, **6**, 614 (1925).

⁵ C. T. Zahn: *Phys. Rev.*, (2) **35**, 848 (1930).

where K is the dielectric constant, R the gas constant per mol, T the absolute temperature, and A and B the Debye constants. p' is the ideal pressure obtained from the approximate van der Waals' equation and is given by

$$p' = p \left\{ 1 + \frac{p}{RT} \left(\frac{a}{RT} - b \right) \right\}$$

From Debye's equation it is seen that at a constant temperature $3(K - 1)/(K + 2)$ should vary linearly with p' . Furthermore, if the quantity $3(K - 1)/(K + 2)$ is plotted against p' for various temperatures, the slopes of the resulting straight lines multiplied by RT^2 give values of $AT + B$ for various temperatures. By plotting these values of $AT + B$ against T , a straight line of slope A and intercept B should be obtained. From B , the electric moment of the molecule may be calculated.

Since no complete data on ethyl alcohol vapor have been obtained, it was considered worth while to study the variation of the dielectric constant with pressure at a number of different temperatures. The value of the electric moment calculated from such data should be the most reliable so far obtained. That the relation between $3(K - 1)/(K + 2)$ and p' might not be entirely linear was indicated by work by Zahn⁶ and Wolf⁷ on water vapor and by Maske⁸ on benzophenone. They found the slopes of the lines increased quite markedly at some "critical" pressure. Zahn and Maske attributed this anomalous effect to the adsorption of the vapor on the condenser plates, while Wolf attributed it to the increased conductivity of the test condenser due to adsorbed vapor on the solid insulators. In view of the findings of Wolf, it was thought advisable to make complete conductivity measurements along with the dielectric constant measurements.

Experimental Method

The dielectric constant measurements were made by the usual heterodyne beat method.⁹ Since in the case of vapors the capacity changes to be measured may be as small as a few hundredths micro-micro-farads, it was necessary to place a smaller condenser in series with the variable precision condenser. This series arrangement was placed in parallel with the test condenser (Fig. 1). The capacity of the series condenser C_s was determined by placing a standard variable precision condenser C'_p in parallel with the test condenser. Known variations were made in C'_p and then the original capacity of the circuit restored by making equivalent changes in C_p . By properly setting the variable air condenser C_1 , it was possible to vary C'_p by small consecutive steps until the entire scale of C_p had been covered. Several hundred different capacity changes were thus measured. From these data a curve was plotted of known capacity changes of C'_p against corresponding capacities of C_p . Known sets of values of ΔC_p , $\Delta C'_p$, and C_p were taken from the curve and the

⁶ C. T. Zahn: *Phys. Rev.*, (2) **27**, 329 (1926).

⁷ K. Wolf: *Anl. Physik*, (4) **83**, 884 (1927).

⁸ F. Maske: *Physik. Z.*, **28**, 533 (1927).

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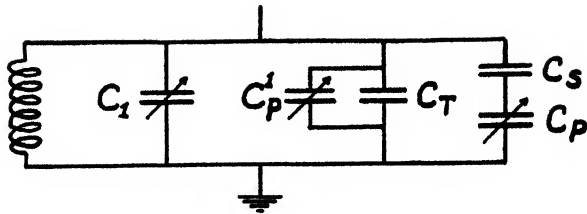


FIG. 1

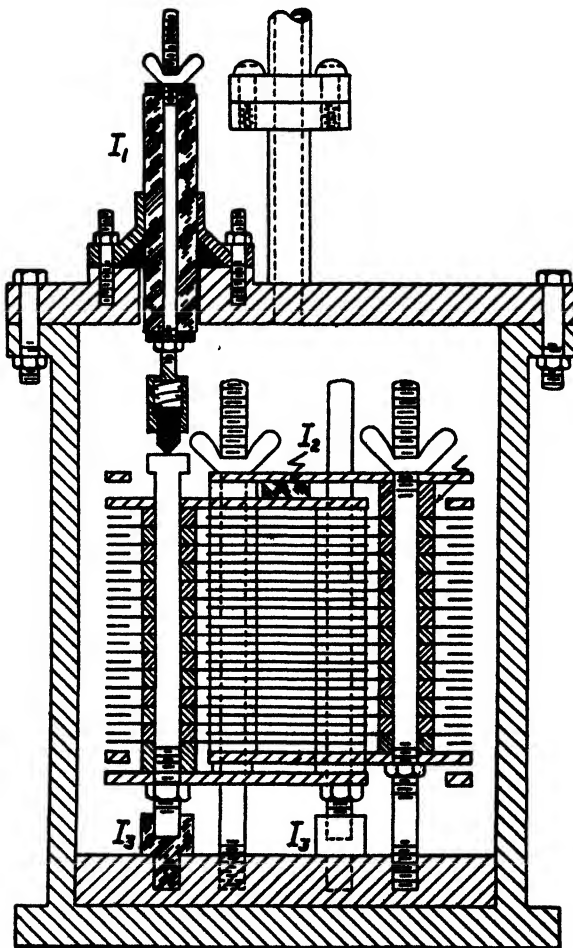
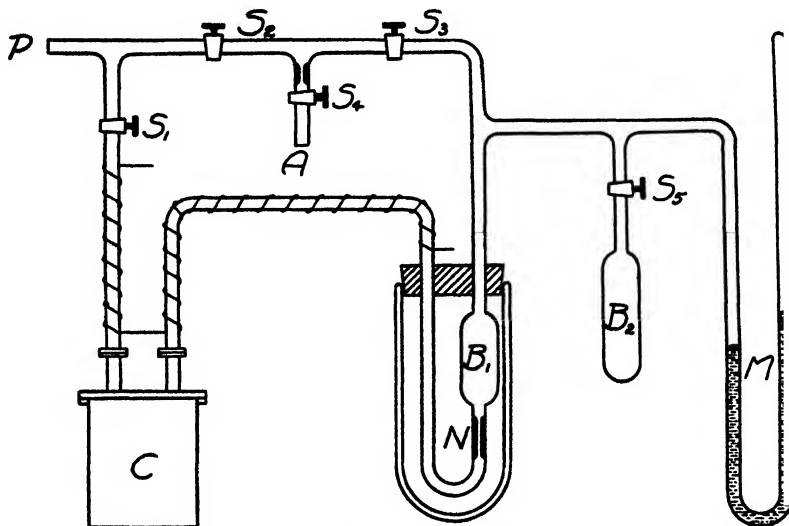


FIG. 2

Cross-section of test condenser

corresponding values of C_s calculated. It is interesting to note that the average value of C_s thus obtained differed by over 10% from that obtained by direct measurement. The difference was due to the fact that when measured directly, one terminal of C_s was grounded, while in the method used neither terminal was grounded. Since in use neither terminal of C_s was grounded, this method of calibration was necessary.

The precision condensers were type 222, General Radio condensers, and were calibrated by measuring the capacity change for every hundred divisions in terms of a fixed interval on another similar precision condenser placed in



VAPOR SYSTEM

FIG. 3

parallel. The worm gear was checked in a similar manner. Capacity changes as measured on C_p should be in error by less than .06 m.m.f.

The test condenser (Fig. 2) was constructed of $\frac{1}{4}$ " brass tubing with $\frac{3}{8}$ " bottom and lid. All joints were silver soldered. The two sets of circular brass plates were supported from a heavy brass disc set in the bottom of the container. The plates were spaced by means of brass washers. The insulated set of plates was held rigid by means of the three solid insulators I_3 and the one insulator I_2 . The lid and insulator I_1 were made airtight by the use of lead gaskets. This construction allowed the changing of the plate spacing, the plate material, and the material of the solid insulators. The capacity of the test condenser was about 940 m.m.f. The distributed capacity of the test condenser was obtained by measuring the capacity of the leads with the circuit open at the inner end of I_1 . I_2 was the only solid insulator in the electric field inside of the condenser, and the unchanged capacity due to it was calculated from geometric considerations. The test condenser was immersed in a thermally insulated constant temperature oil bath. Temperatures were measured with a platinum resistance thermometer.

The vapor system (Fig. 3) was similar to the one used by Miles.³ It had the advantage of two exhausts in the test condenser, one exhausting on each side of the liquid ethyl alcohol contained in the U-tube at B_1 . Any air which might enter the test condenser around the U-tube, due to too violent boiling of the alcohol in the heated arm of the U, could be immediately removed by evacuation through the cock S_1 . The measurement of the change in the capacity of the test condenser caused by evacuation was made immediately after the reading at any given pressure was taken. This tended further to eliminate any error which might have been introduced by any gradual changes in the electric circuits. The bulb B_1 and U-tube were immersed in a dry ice bath which maintained a temperature between -70°C and -80°C . Both an organic and an inorganic stopcock lubricant were used, and no effect of either was detected in the results.

The resistance of the test condenser was measured by charging it to a known potential and allowing it to discharge through its leakage resistance, the change in potential being determined with an electroscope.

The ethyl alcohol was prepared from the commercially pure product. It was carefully dried by reflux distillation for twenty-four hours over calcium oxide and then distilled off, the middle fraction only being used. All samples of alcohol used were tested for the presence of water with anhydrous copper sulphate.

Data and Results

The first set of measurements (Table I) was taken at a temperature of 24.55°C , which was the lowest temperature at which the oil bath could be maintained conveniently without some special means of cooling. Data were taken for pressures varying from 2 mm to near saturation, which in this case was about 5.8 cm of Hg. The solid insulators were of Pyrex. The values of p and p' , and of $(K - 1)$ and $3(K - 1)/(K + 2)$ are essentially the same at the low pressures used here. The curve (Fig. 4) of $3(K - 1)/(K + 2)$ plotted against p' is a straight line from a pressure of 2 mm to within about 1 mm of saturation. The curves for 46.55°C , 58.90°C , and 74.72°C (Fig. 5) are also linear from pressures of a few millimeters to near saturation. However, near saturation, the slopes of the lines increase very abruptly. This occurs at a pressure about 1.5 cms of Hg. below saturation at 58.9°C , and about 2 cms below saturation at 74.7°C . These changes in slope appear to be similar to the ones found by Zahn and Wolf in the case of water vapor, except that there is no marked tendency for this effect to disappear as the temperature is raised. The remaining data in Table I were taken at temperatures above the normal boiling point of ethyl alcohol, so saturation pressures were not reached. As would be expected, the curves were linear over their entire extent. The slopes of the lines corresponding to temperatures of 137.8°C and 170.5°C were determined by taking the average of a number of readings taken at approximately one pressure.

The resistance data for the test condenser with Pyrex insulators are shown in Fig. 6. The resistance is seen to decrease quite markedly as the saturation

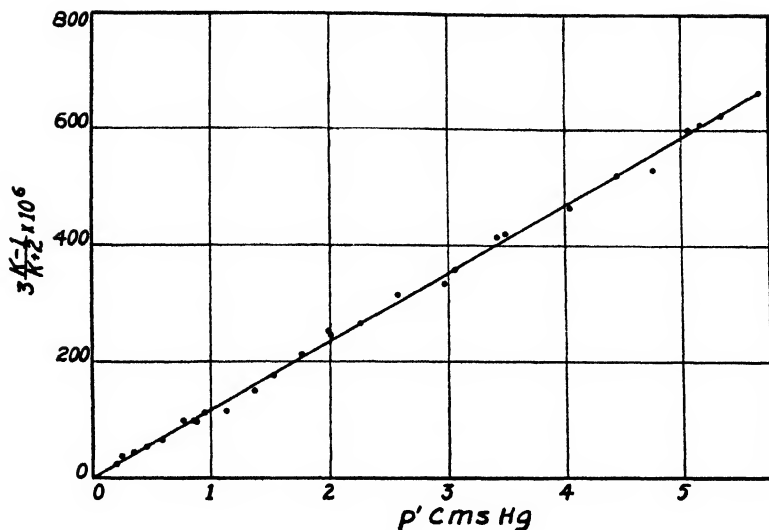


FIG. 4

The variation of polarization with the corrected pressure, p' , for ethyl alcohol vapor at a temperature of 24.55°C.

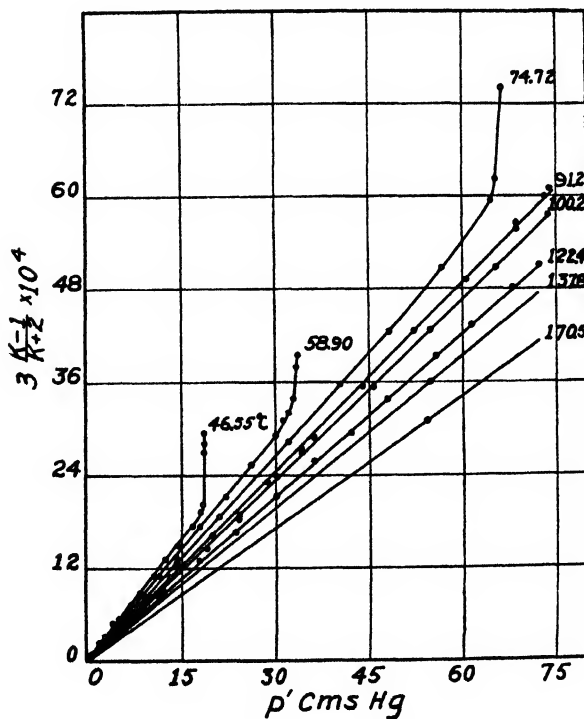


FIG. 5

The variation of polarization with the corrected pressure, p' , for ethyl alcohol vapor, using Pyrex insulators. Temperatures range from 46.55°C to 170.5°C.

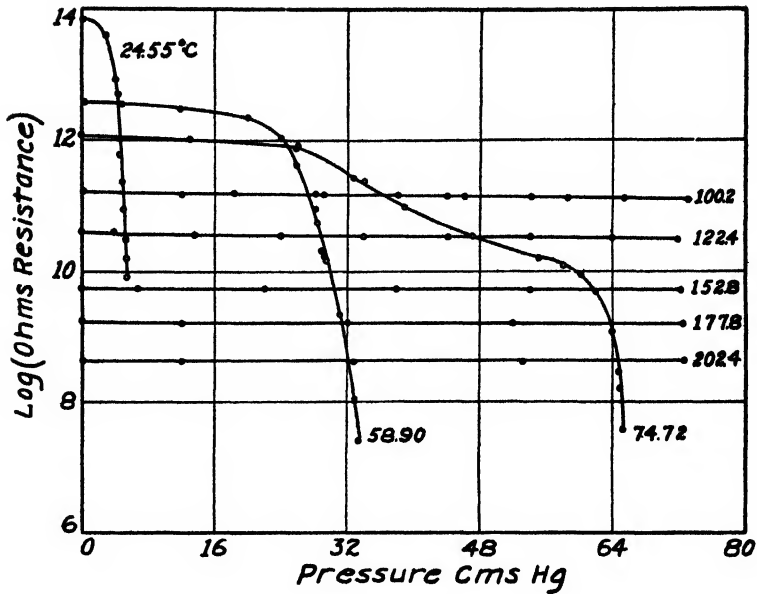


FIG. 6
The dependence of test condenser resistance upon vapor pressure at various temperatures, using Pyrex insulators.

TABLE I*
Summary of Dielectric Constant Data

	t°C	T°K	$\frac{(K-1) \times 10^6}{p}$	$3 \frac{K-1}{K+2} \times \frac{10^6}{p'}$	AT+B
**	24.55	297.5	117.3	117.2	64,990
	46.55	319.5	103.0	102.6	65,650
	58.90	381.9	96.0	95.5	65,960
	74.72	347.7	88.5	87.9	66,600
	91.20	364.2	82.2	81.4	67,670
	100.2	373.2	78.7	77.9	68,000
	122.4	395.4	70.6	70.0	68,570
	137.8	410.8	65.9	65.6	69,640
	170.5	443.5	57.6	57.3	70,580
***	58.90	381.9	96.0	95.5	65,960
	74.72	347.7	88.5	87.9	66,600
	177.1	450.1	56.1	55.8	70,920

* p and p' in cms of Hg.
** Data taken with Pyrex insulators.
*** Data taken with quartz insulators.

pressure is approached. At higher temperatures where the pressures are below saturation, the relation between the logarithm of the resistance and the vapor pressure is practically a linear one.

The Pyrex insulators in the test condenser were next replaced by fused quartz, and dielectric constant data were taken for three temperatures. The curves are shown in Fig. 7. The marked change in slope found previously with the Pyrex is nearly absent. This can be distinctly seen in Fig. 8 where data obtained with both insulators at the same temperature are plotted on a

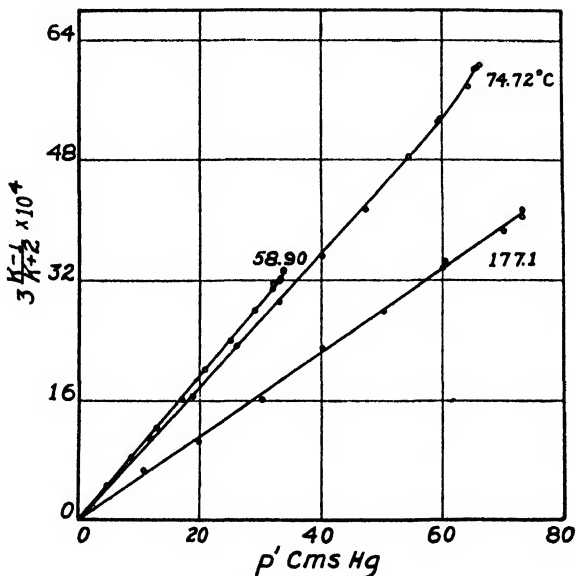


FIG. 7

Variation of polarization with the pressure, p' , at various temperatures, using quartz insulators.

single curve. The resistance curves are essentially of the same form as found for the Pyrex. In the vicinity of the saturation pressure the resistance in the case of the quartz was higher by a factor of about ten.

In order to obtain the value of the electric moment of the ethyl alcohol molecule, a curve was plotted of $3(K-1).RT^2/(K+2)p'$ against the absolute temperature. The slopes of the lower linear parts of the dielectric constant versus pressure curves were multiplied by RT^2 to obtain $AT+B$. These values are tabulated in Table I and the curve is shown in Fig. 9. The maximum deviation of any of the twelve points from the Debye straight line is less than .5%. The value of the intercept as calculated by the method of least squares was 52,650 and the value of the electric moment was 1.68×10^{-18} . This value compares quite favorably with Miles's value of 1.69 and rules out definitely Sanger's value of 1.11.

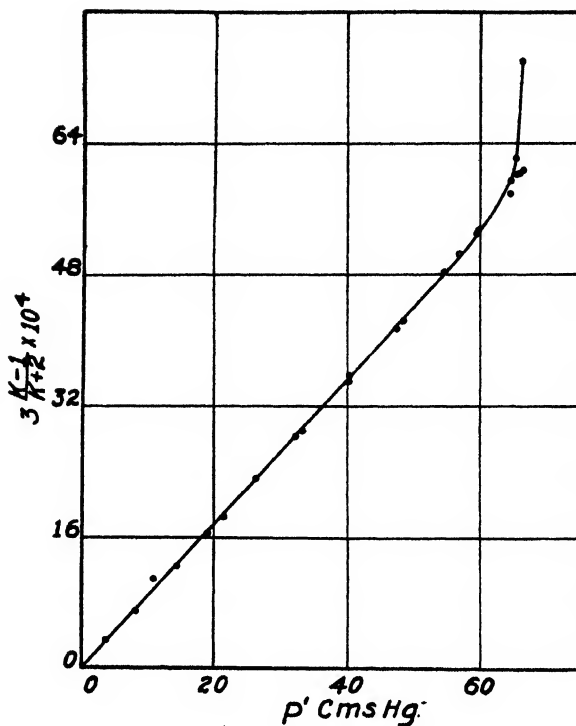


FIG. 8

Variation of polarization with the pressure, p' , at 74.72°C . Data obtained with quartz insulators are shown by the solid dots, and data obtained with Pyrex insulators by the circles.

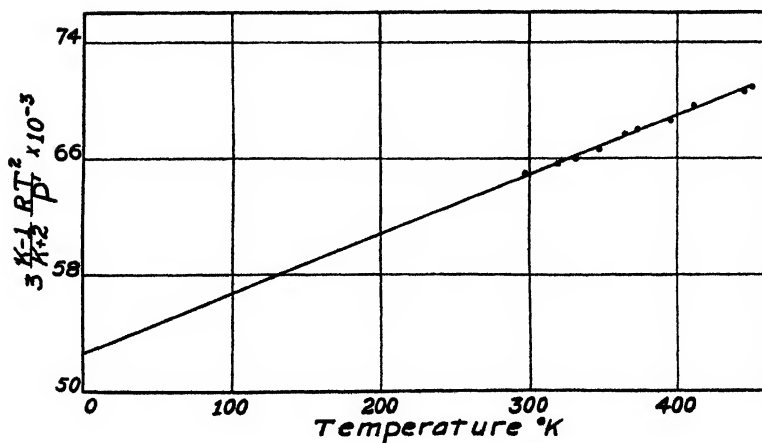


FIG. 9

Debye line for ethyl alcohol vapor.

Possible Effect of Conductivity

It was desired to determine both experimentally and theoretically if the lowered leakage resistance of the test condenser near the saturation vapor pressure could account for the observed deviations in the dielectric constant curves. To determine this theoretically, the effect of the leakage resistance on the output circuit of the oscillator was considered. The output circuit may be considered as containing in place of a triode an alternator of generated e.m.f. E and resistance R_p connected in series with a parallel combination of three branches. One branch contains an inductance coil of resistance R_L and reactance X_L , the second branch is the condenser leakage resistance R_c and the third branch contains the condenser having a reactance X_c . By applying Kirchhoff's laws, an expression may be obtained for the current I_L through the inductive branch in terms of the constants of the circuit and the e.m.f. E . If the grid current be neglected, E may now be expressed in terms of the amplification factor of the tube, the mutual inductance between the grid and plate circuit inductance coils, and the current I_L through the coil in the plate circuit. By combining these two equations for the current I_L through the inductive branch, both E and I_L are eliminated. A resultant expression containing only constants of the circuit may be obtained by equating the imaginary parts in the equation. When solved for the capacity C , this expression becomes

$$C = \left\{ 1 + R_L \left(\frac{1}{R_c} + \frac{1}{R_p} \right) \right\} \frac{1}{2\pi f X_L}$$

Since the frequency of the oscillator is maintained constant at about 500 kilocycles, and X_L and R_L do not change, changes in R_c or R_p must be compensated for by changes in the capacity C . The values of R_p and R_L are approximately 2×10^4 and 10 ohms, respectively, and X_L is 310 ohms. Then to maintain a constant frequency, the change in capacity occasioned by the decrease in R_c from 10^{13} to 10^8 ohms, is 10^{-4} m.m.f. This change is entirely too small to account for the observed dielectric constant deviations, since at 58.90°C at a vapor pressure corresponding to a test condenser resistance of 10^8 ohms, a capacity change of 3300×10^{-4} m.m.f. is necessary. Furthermore, this change in capacity is not only too small, but in the wrong direction. When the test condenser is evacuated, its capacity is a minimum and the capacity of the parallel precision condenser (Fig. 1) is a maximum. R_c is also a maximum. The introduction of the vapor increases the test condenser capacity on account of its dielectric effect and, consequently, the precision condenser capacity must be decreased to maintain a constant frequency. However, the introduction of the vapor causes a decrease in R_c which necessitates a slight increase in the total capacity to maintain a constant frequency, as seen above. Therefore, the precision condenser capacity change will not be as large as it would have been if the resistance had not been lowered. Consequently, the calculated dielectric constant would be too small.

In the above equation it is seen, however, that any change in R_p caused by a change in R_c would be quite noticeable, due to the fact that R_p^{-1} is greater than R_c^{-1} by a factor of 10^4 . In order to determine how effective the changes

in R_c might be in changing R_p , an expression was obtained for the total impedance of the three parallel branches. X_c was eliminated from this expression by means of the above equation for C . The resultant expression for the total impedance is

$$Z = \frac{R_c X_L^2 (X_L^2 + R_L R_c + R_L^2) - j R_L R_c^2 X_L [R_L (1 + R_L B) + X_L^2 B]}{R_c R_L [R_L R_c (1 + R_L B)^2 + 2 X_L^2] + (R_L R_c X_L B)^2 + X_L^2 (R_L^2 + X_L^2)}$$

where $B = 1/R_c + 1/R_p$.

While it is not possible to calculate R_L exactly, its value is probably between 5 and 10 ohms. Taking the value of R_L as 10 ohms and that of X_L as 310 ohms, the effect on Z of lowering R_c to 10^8 ohms is practically negligible, being 1 part in 10,000. The fractional change in phase angle is entirely negligible. If R_L is taken as 5 ohms, the fractional change in Z introduced is 1 part in 7000 and the phase angle is changed by 1 part in 8000. Certainly any change in R_p due to such a small change in Z would be entirely negligible. This conclusion is in agreement with experimental data on the type of tube used, which show that a change of 1 ohm in load resistance causes a change of about .5 ohms in plate resistance at the plate voltage used. This change in R_p , together with the corresponding change in R_c cause a change in capacity of 1.1×10^{-4} m.m.f., as calculated from the preceding expression for the capacity C . This differs very little from the previous value obtained by neglecting changes in R_p .

In deriving the expression for the capacity C , the input capacity of the triode was neglected. The five-mesh network including the grid-plate and grid-filament capacities cannot be solved readily as in the previous case, as the equations become too long and cumbersome. It seems doubtful though that the above results would be greatly affected by considering the tube capacity, since the change in effective input capacity caused by the changes in R_c and R_p is only 10^{-3} m.m.f.

A direct measurement of the effect of a leakage resistance is difficult to make, since the change in the actual distributed capacity of the system caused by switching in a resistance is quite likely to mask entirely the leakage effect. For this reason, there may be some question about such measurements as were made by Wolf.⁷ In the present case the effects of a number of different, though geometrically duplicate, resistances were measured. These resistances were introduced singly in parallel with the evacuated test condenser. While the distributed capacity change introduced was by no means negligible, it should have been practically the same for the different resistances. The resistances used varied from 10^4 to 10^7 ohms. Between 5×10^5 and 10^7 ohms, the effective capacity of the circuit was increased by from 0 to .2 m.m.f. Between 5×10^5 and 10^4 ohms, the effective capacity was decreased by the introduction of the resistance by from 0 to 9 m.m.f. The increase in effective capacity at high resistance is doubtless due to the actual capacity introduced by the resistance used. The effect of the resistance is apparently to decrease the effective capacity of the circuit, the effect being much more pronounced at low resistance. At 10^7 ohms, the increase in capacity is too small to account

for the observed dielectric constant deviations, even though it be assumed (which is certainly not the case) that the capacity increase is due to the resistance effect alone.

The author is fully convinced from his observations that the direct current leakage resistance of the test condenser cannot account quantitatively for the observed deviation from the Debye straight line near saturation. On the other hand, he is fully convinced that there exists a very intimate connection between this leakage resistance and the deviation. The fact that the resistance curves show marked breaks at the same vapor pressures as do the dielectric curves strongly indicates a close connection. If the deviations in dielectric data are to be accounted for directly and quantitatively by the leakage resistance of the test condenser, then the author feels that the magnitude of the leakage resistance at high frequency and the effect of this upon the condenser capacity must be distinctly different from that observed with a direct potential.

Summary and Conclusions

A method was used for calibrating the series condenser directly as it was to be used in series with the precision condenser. This eliminated the error present in the common method of measurement in which one terminal of the series condenser is grounded during the calibration, but not grounded when in use. The error thus eliminated was found experimentally to be quite appreciable, as much as 20% in $(K - 1)$ in some cases.

The vapor system was so arranged that the dielectric measurements were relatively independent of any gradual variations in the electrical system, since the readings for any given pressure were all taken within two minutes once equilibrium had been reached. Any air admitted into the test condenser either by a leak or around through the U-tube due to too violent boiling at the heated surface was readily removed after each reading since the test condenser was completely evacuated directly.

The relation between $3(K - 1)/(K + 2)$ and the corrected pressure p' was found to be linear at all temperatures, except near the saturation vapor pressure.

The direct current resistance of the test condenser filled with vapor was found to decrease very rapidly as the saturation pressure was approached. The resistance in the case of quartz was found to be slightly higher than for Pyrex.

The breaks in the dielectric constant curves cannot be explained quantitatively by calculating the effect of the leakage resistance upon the effective capacity of the oscillatory circuit. The calculated effect is much too small, and in the wrong direction. However, since the dielectric constant and resistance curves have breaks at approximately the same pressures, it seems quite probable that the two effects are quite closely related.

Direct measurements upon the effect of a leakage resistance seem to show that the effect of the resistance is entirely too small and in the wrong direction to account for the observed deviations in the dielectric constant curves.

The observed points of $3(K-1)RT^2/(K+2)p'$ as determined from the slopes of the pressure curves, when plotted against the absolute temperature, fall closely on the Debye straight line. There is no marked deviation found at the lower temperatures, as was found by Miles⁷ at a temperature of 351°K, although four readings were taken at temperatures lower than this. Thus Miles' assumption of association seems to have little foundation. Also, Sanger's⁸ curve which showed a marked deviation from the Debye straight line is at variance with the present results. In the present work no one of the twelve points obtained falls as much as .5% from the straight line drawn through the points.

In conclusion, the writer wishes to thank Dr. J. D. Stranathan, under whose direction this problem was undertaken, for his continued assistance throughout the work, and Dr. H. H. Germond, for his valuable suggestions.

THE BEHAVIOR OF METALLIC SOAPS WITH ORGANIC SOLVENTS

BY JAMES W. MCBAIN AND WINIFRED L. McCLATCHIE

One of us¹ pointed out that the behavior of soaps towards aqueous solution demonstrated the thermodynamic stability of the colloidal state for certain cases as compared with crystalloidal and crystalline states. This view has apparently been accepted as regards many sols. However, it has been questioned as applicable to jellies. It is, therefore, of interest to see in how far a spontaneous formation of jellies from crystalline material and pure solvents can occur. Such instances are encountered amongst soaps in contact with organic solvents. Within a very narrow range of temperature and concentration this has been reported for sodium oleate and water.²

Again, very little work has been done on jellies of known chemical formula like soaps and in non-ionizing media where ionic and Donnan equilibria are eliminated and where the results gain significance from the simplicity of the conditions.

To create a jelly, molecules must organize. In a stable sol this is done by the spontaneous formation of colloidal particles, each consisting of an orderly array of molecules whose relative positions are a result of the characteristic properties of the different groups in each molecule. For a jelly something more is required; some structure must be built up from the separate micelles.³ For supermolecules of a chain-like nature juxtaposition might suffice. In all cases there must be an affinity between the solvent and some grouping of the molecule exposed in the micelle. Swelling will be due to two separate causes. First, direct combination, sorption, or polarization of molecules, or clusters or strings of molecules of solvent with the exposed groupings. Second, through the penetration of free molecules of solvent between the interlacing structures to release strains and tensions in the structure, because close packing will not in general accord with the undistorted shape and arrangement of molecules and micelles. The first factor in swelling will correspond to the thermodynamic properties represented by the vapor pressure of the solvent in the system. The second, when present, will give rise to an additional swelling pressure of as purely mechanical origin as the familiar spontaneous refilling of a rubber tube with air after the tube has been squeezed, the pressure released, and the ends opened to the atmosphere. This second process is well demonstrated by the observations of Stamberger and Blow⁴ on the swelling of vulcanized and unvulcanized rubber. Swelling

¹ J. W. McBain: Colloid Symposium Monograph (Cambridge, 1926), 4, 1 (1926).

² M. E. Laing and J. W. McBain: *J. Chem. Soc.*, 117, 1506 (1920).

³ Compare J. W. McBain: *J. Phys. Chem.*, 30, 239 (1926); *Trans. Faraday Soc.*, 20, 22 (1924).

⁴ P. Stamberger and C. M. Blow: *Nature*, 124, 13 (1929); *Rubber Chem. Tech.*, 2, 591 (1929).

pressure will correspond to vapour pressure only when there is no such structural factor to consider. The thermodynamic equation assumes that all of the pressure applied to the jelly is effectively transmitted to the solvent, for it is the pressure on the solvent that is given by the equation. For this reason calculated values for swelling pressures may be expected to be less than experimental values.

The first step when a crystal is placed in contact with a solution is the separation of the molecules by molecules of solvent. If this process is complete, they pass into solution. But concurrently micelles may be organized. If they are largely separated they pass into solution as a sol. If they are not sufficiently separated they merely form a swollen mass below the liquid. If the packing of the molecules in the crystal is sufficiently dense and the constitution such that lyophilic groups are not exposed to the solvent, the crystal will appear nearly insoluble and it will not swell.

It is quite otherwise with the solid produced after the crystal has been once brought into solution, as for example by heating, and then dried. The dried mass now retains something of the organization of a jelly and it must swell when placed in contact with cold solvent. The first stage in swelling must then occur, due to a forcing apart of the micellar units existing in the dried jelly through the affinity between solvent and lyophilic groups. This, owing to the minute dimensions of the structure, could produce a very appreciable increase in volume. The question as to whether or not swelling will be followed by the micelles passing into solution as a sol depends upon the balance of forces previously mentioned between the cohesive groups for each other and for solvent. A decisive factor is concentration, a certain minimum concentration of micelles being required to form a coherent jelly or gel. For example, this is 12 per cent for aluminium dipalmitate in dry xylene to form a clear firm jelly. Another decisive factor is temperature. With our systems the higher the temperature, the more complete the interaction between solvent and solute. Thus at sufficiently low temperatures the interaction may be so suppressed that there is little or no swelling, whereas at sufficiently high temperatures a fully formed jelly will disintegrate to separate micelles and these will tend ultimately to separate into single molecules.

Instances of each of the kinds of behavior outlined in the foregoing paragraph are to be found in the case of soaps and organic solvents.

It will be noted that the comprehensive scheme outlined above includes agreement with the views put forward by Whitby¹ in 1926 on page 216 of his paper but not with those he presents on pages 218 and 219. He has made the assumption that all of the solvent imbibed by a swelling colloid is due to solvation, quoting examples of the taking up during swelling as much as 20-40 times more solvent than the original weight of solid. It is indicated above how and why only a small proportion of it need be so regarded. The slightest pressure or, in some of our cases, a slight lowering of temperature serves to liberate large portions of the imbibed solvent, showing how negligible must be the chemical affinity. Whitby is too much inclined to consider

¹ G. S. Whitby: Colloid Symposium Monograph (Cambridge, 1926), 4, 216 (1926).

that McBain's point of view depends solely upon the results of sorption experiments, not weighing as well the arguments from the mechanical explanations and models of apparent viscosity.

As regards the argument used by Whitby and others that no particles are visible in benzene solution of rubber when examined with the ultramicroscope, it may be pointed out that in 1925 McBain and Dr. H. Harris examined with the best ultramicroscopes then available all of the clear and transparent aqueous jellies which had been described in the literature up to that time, and they found that all jellies can be prepared so clear that they cannot be resolved in the ultramicroscope, just as in the case of very fine gold sols where only a Tyndall cone remains. This does not mean that in dilute jellies such substances as, for example, manganese arsenate and zinc arsenate are to be regarded as having combined with all the water present but rather that the degree of dispersion is exceedingly fine. Indeed, in many cases envisaged above, it might be molecular without the molecules losing their coherence with other molecules at portions of their surface. One need only recall in this connection the possibilities opened by the work of Sheppard, Nietz, Keenan, Devaux, Gorter, Grendel, Zocher, etc., who have shown that various colloids of high molecular or micellar weight such as proteins, rubber, etc. can spread as coherent films on surfaces of mercury or of water to such large areas that their average thickness is only a few Ångstrom units. Indeed, the term degree of dispersion as ordinarily used has lost most of its significance on account of the great rarity of completely independent primary particles. A sol or a jelly of ferric hydroxide can easily be made so clear that it is not resolved in the ultramicroscope and yet unable to pass through the pores of ordinary filter paper.

Enormous solvation is assumed by many writers in trying to explain why such colloids are not resolvable in the ultramicroscope by making the further assumption that the colloidal particles are thereby so diluted that their refractive index approaches that of the solvent itself. This hypothesis is forced and wholly unnecessary. Even gold particles whose interior is crystalline and whose refractive index differs ever so much more from that of water cannot be resolved in the ultramicroscope if they are less than about 40 Å in diameter.

Few seemed to have followed our argument, repeatedly put forward, that if a jelly can be prepared thus optically clear without losing any of its characteristic properties, the significant properties of the jelly must be due to the invisible particles. Even when the jelly, less carefully prepared, shows a number of resolvable particles, these do not constitute its structure and the fact that they may be more or less distant from each other possesses no particular meaning and does not disprove the conception of jelly structure as due to interlocking of the unresolved and unresolvable particles.

The present summary of observations made in 1929¹ is part of a search for a suitable pure chemical substance for quantitative study of jellies in

¹ Miss W. L. McClatchie, Thesis for the degree of Master of Arts, Stanford University, December, 1929. A few months later M. H. Fischer and M. O. Hooker (*Kolloid-Z.*, 51, 39 (1930)) published observations which supplement those given here.

non-aqueous solutions. It concerns twenty soaps with xylene, and for silver, sodium, and aluminium palmitates about fourteen other solvents.

Preparation of Soaps

Silver palmitate was made by mixing a solution of silver nitrate in alcohol with excess of hot alcoholic solution of palmitic acid, washing the precipitate with 95 per cent alcohol and with ether. On ignition 29.7 and 29.5 per cent of silver (theoretical being 29.7 per cent) was obtained. Thorium palmitate was similarly prepared.

Most of the soaps were prepared by precipitation of sodium soaps from aqueous solution. The sodium and potassium soaps were especially made for us by Kahlbaum. We have pointed out elsewhere¹ that normal aluminium soaps such as tripalmitate do not exist but that if prepared in contact with aqueous solution the amount of combined fatty acid does not much exceed the monobasic compound, and even if prepared most carefully in anhydrous solvents with excess of fatty acid, there are not more than two equivalents of combined fatty acid in the molecule.

It is, of course, of direct significance in the wedge orientation theory of emulsions where the aluminium palmitate has been erroneously assumed to be a tribasic soap although the conditions are ideal for hydrolysis and abstraction of the fatty acid even had the tribasic soap been originally capable of existence.

Behavior towards Xylene

For a given soap the swelling increases with increase in temperature. At a given temperature the swelling of soaps with the same cation increases with increasing molecular weight and is greater for soaps of unsaturated than for soaps of saturated fatty acids. For different soaps of the same fatty acid there is a tendency towards increased swelling with increased valency of the cation and, with exceptions, with increased atomic weight.

I. Soaps that do not go into solution in xylene at 25°, give no evidence of swelling when the solvent is heated, but are quite soluble in the boiling solvent, and reprecipitate without evidence of jelly formation on cooling are: zinc stearate, copper palmitate, ferrous palmitate, and thallous palmitate. Lead palmitate probably belongs in this group.

II. Soaps that do not go into solution in xylene at 25° and show only slight swelling in the boiling solvent, remaining insoluble, are: sodium laurate, potassium palmitate, ferric oleate, and barium palmitate. Barium palmitate, in spite of its insolubility in boiling xylene, and its inability to form a jelly at any temperature, swells very appreciably in contact with hot xylene.

III. Soaps that do not go into solution in xylene at 25° but swell and go into solution on heating and set to fairly firm jellies when cooled are: thorium palmitate and silver palmitate. A 0.2-0.5 per cent jelly of silver palmitate remains unaltered for weeks. It remains clear and becomes more elastic as nine tenths of the solvent is squeezed out by mechanical pressure. Thin

¹ J. W. McBain and W. L. McClatchie: Accepted by J. Am. Chem. Soc. for August 1932.

sheets of dried jelly increased in length and breadth by one third when exposed to xylene.

IV. Soaps that do not go into solution in xylene at 25°, swell and form elastic jellies when heated to about 100°, but undergo syneresis on cooling are listed as follows in approximate order of increasing swelling at room temperature: lithium palmitate, sodium palmitate, potassium oleate, sodium stearate, calcium palmitate, sodium oleate, sodium erucate, and chromium palmitate. Dried samples of these jellies swell somewhat in xylene at 25°. In 1925 one of us (J. W. M.) with Dr. H. Harris found that Kahlbaum's sodium stearate heated in a closed tube with benzene to 105°-110° forms a transparent jelly which is seen to be isotropic between crossed nicols. Just below 105° crystallization sets in, liberating liquid. With a rise of temperature the jelly reforms and is therefore the most stable state above 105°. The jelly is homogeneous and elastic. With lemonene the behavior is exactly similar but the transition slower. Sodium oleate behaves similarly with benzene and xylene, but neither soap exhibited any signs of gelation with acetone or chloroform. We found that von Weimarn¹ had already described in detail similar observations with sodium oleate in toluene, xylene, and benzene as well as in cumene and cymene.² Some of his jellies of sodium oleate were so elastic that a rod of jelly could be bent into a complete circle and again resume its original form on release. Camphoryl phenyl thiosemicarbazide (like the arsenates or dibenzyl cystine with water) is quite different from our soaps in that the crystalline state is the stable one in the presence of toluene, benzene, ether, chloroform, and alcohol. We found that a jelly could be produced from a slight supersaturation, whereas von Weimarn has postulated large supersaturation as a necessary condition for gelation.

Sodium palmitate powder is unaffected by cold xylene but swells and becomes transparent on heating, dispersing to a very viscous sol much as described by von Weimarn for sodium oleate. On continued heating it sets to a quite stiff, transparent, elastic jelly between the concentrations 1 and 8 per cent. On cooling the jelly undergoes strong syneresis and breaks up entirely into small pieces on shaking. A nearly transparent sheet dried at 100° became more transparent and increased 30 per cent in weight through 18 hours contact with xylene at 20°. Such a sheet swelled twenty fold in three hours when exposed to the vapor of boiling xylene and was still swelling rapidly. Sodium stearate was similar to sodium palmitate with less syneresis and greater swelling at room temperature (90 per cent in 24 hours).

A still completely transparent sheet of sodium oleate jelly dried at 100° was brittle and non-elastic but increased in weight on contact with xylene at room temperature by 50 per cent in 2 hours and 150 per cent in 36 hours, giving a transparent, somewhat flexible jelly. Sodium erucate was similar with greater swelling of preformed jelly although the original sodium erucate was not affected by cold xylene in 2 days; at 40° it nearly doubles its volume in a few hours.

¹ P. P. von Weimarn: "Die Allgemeinheit des Kolloidzustandes," Bd. I, 2 Aufl., 352-363 (1925); J. Russ. Phys.-Chem. Soc., 46, 610, 624, 625 (1914); 47, 2163 (1915).

² P. P. von Weimarn: J. Russ. Phys.-Chem. Soc., 48, 532 (1916).

Calcium palmitate in the form of dried jelly did not swell in contact with xylene at room temperature. Chromium palmitate, however, swelled by 160 per cent in 4 hours under the same conditions.

V. Soaps that swell on heating at lower temperature than those of group IV, giving fairly fluid solutions in boiling xylene and setting to jellies, which undergo syneresis if cooled to sufficiently low temperatures, are: aluminium stearate, aluminium palmitate, and aluminium oleate (the only soap that swells without limit at room temperature). Dried samples of the jellies swell at room temperature. Aluminium stearate does not swell below about 50°. A dried sheet of jelly swelled 20 per cent in one hour, 50 per cent in 2 hours, at room temperature. Aluminium oleate, as dried jelly, swelled 190 per cent in half an hour at room temperature, being completely converted to a sol in a few days.

Aluminium Palmitate in Xylene¹

50° is a somewhat characteristic temperature because when a 4 per cent mixture of the impure monopalmitate prepared from aqueous solution is warmed, it is at this temperature that the entire mixture, which has progressively swelled, forms a fairly firm, elastic, extensible jelly. At the boiling point, even a 10 per cent jelly shows unusual ability to flow. Cooled to -15°, however, 1-10 per cent jellies are firm and elastic, do not flow, but show syneresis, the liquid being not fully reimbibed until the samples are warmed to nearly 50°. This parallels the well-known hysteresis of aqueous gelatin or agar but with a much greater range. The jellies are quite unusually elastic. A jelly dried at 100° is completely transparent and during a two hours' contact with xylene increases in weight by 40 per cent at 20°, 100 per cent at 25°, 120 per cent at 30°, 600 per cent at 40°, and 900 per cent at 60°.

Solvents for Pure Silver Palmitate

I. Solvents in which the soap is insoluble at room temperature, and not appreciably so on heating to about 100° are: diethyl ether and diacetone alcohol.

II. Solvents in which the soap is not appreciably soluble when at room temperature, but is moderately soluble on heating to 100° are: diethylene glycol, cellosolve, α -bromonaphthalin, butyl stearate, benzoyl chloride, xylene, chlorobenzene, and dichlorobenzene. With the last three solvents weak jellies are produced on cooling.

III. A solvent in which the soap is very soluble at room temperature is triethanolamine.

Solvents for Sodium Palmitate

I. Solvents in which the soap is not appreciably soluble at the boiling point of the solvent are: ethyl methyl ketone, benzyl acetate, and benzaldehyde.

¹ E. Markowicz (Farben-Ztg., 34, 326, 414, 503 (1928)) reported that aluminium soaps and resinsates swell in benzene derivatives and their homologues.

II. Solvents in which the soap is soluble at the boiling point, giving at least a 2 per cent solution, but is insoluble or only slightly so at room temperature are: butyl nitrite, butyric acid, and acetophenone.

III. Solvents in which the soap is soluble at the boiling point and which give jellies at room temperature without marked syneresis are: chloracetaldehyde, paraffin oil, and amyl valerate.

IV. Solvents in which the soap swells to a gelatinous mass on heating and undergoes syneresis on cooling to room temperature are: diamyl ether, *o*-dichlorobenzene, bromobenzene, benzene, toluene, and xylene.

Solvents for Aluminium Palmitate

I. Solvents in which the soap is insoluble in both the boiling and cold solvent are: water, ethyl alcohol, amyl alcohol, glycerine, diethyl ether, and acetone.

II. Solvents in which the soap is soluble both at the boiling point and on cooling are: nitrobenzene, amyl valerate, diethyl aniline, diamyl ether, chloroform, *o*-dichlorobenzene, benzene, toluene, and xylene. The last four solvents behave in a manner comparable to that described for xylene.

Conclusions

These experiments indicate that for the silver and aluminium soaps the best solvents are in general the least polar compounds, a result in accord with Whitby's statement¹ that silver soaps swell in rubber solvents. The sodium soaps, although soluble in polar solvents, also dissolve and form jellies in the non-polar solvents. Although a number of solvents were found for silver palmitate, none gave elastic jellies at ordinary temperatures, which usually in previous work with various soaps indicated swelling ability for the combination used.

Sorption Isotherms of Vapors with Aluminium Palmitate

Isotherms at 40° were observed with an aluminium palmitate which after extraction with dried ether contained 6.5 per cent of aluminium and 87.7 per cent fatty acid. It was used in the form of a dried jelly made by dissolving in xylene at 90° and evaporating at 50°, ending with evacuation for 8 hours at 50°-90°. Before inserting into the experimental vessel, they were evacuated for 24 hours and the vessel sealed. A sorption pipette was used of a simpler design than that subsequently published by Jenkins and Bennett.² The necessary corrections are made for the amount of solvent vapor in the dead space. Four or five days were allowed before the attainment of equilibrium in each case. The results are given in Fig. 1.

¹ G. S. Whitby: Colloid Symposium Monograph (Cambridge, 1926), 4, 213 (1926).

² W. J. Jenkins and H. B. Bennett: J. Phys. Chem., 34, 2318 (1930).

It is seen from Fig. 1 that the aluminium soap sorbed distinctly more toluene than benzene and much more chloroform than either. This resembles the order of swelling of rubber in these three solvents. All three curves have the form that one of us has designated¹ as characteristic for vapors of a moderate solvent with a swelling colloid such as the cellulose esters.

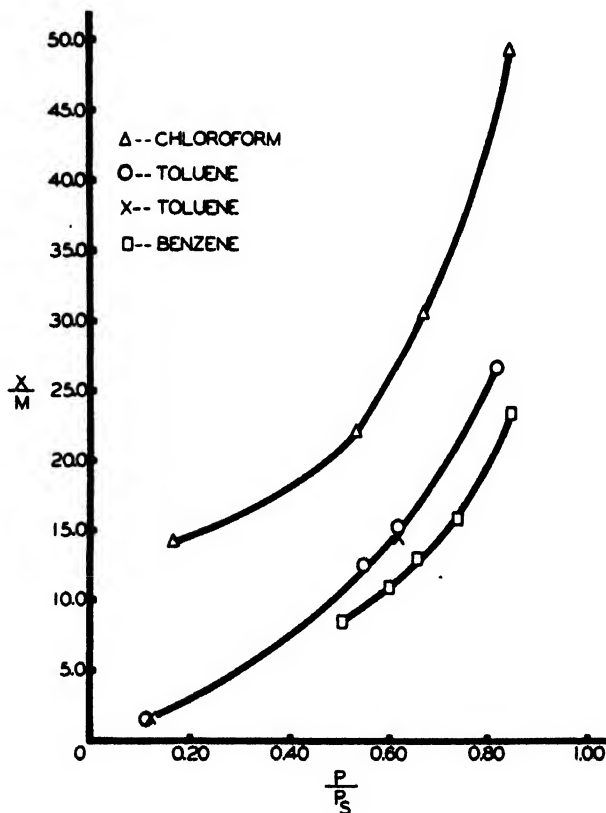


FIG. 1

The sorption of vapors by an aluminium palmitate intermediate between mono- and dipalmitate. Grams sorbed per 100 grams of soap, x/m , are plotted against relative humidities, p/p_s . The two crosses represent points on an independent isotherm with toluene.

Summary

The theory and mechanism of swelling and gelation is discussed. Numerous observations with metallic soaps and organic solvents illustrate theoretical points.

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¹ J. W. McBain: "Sorption of Gases and Vapours by Solids," 372 (1932).

THE SCATTERING OF LIGHT*

BY WILDER D. BANCROFT AND CHARLES GURCHOT

Over sixty years ago Lord Rayleigh¹ worked out a theory for the color of light scattered by fine particles. "It is now, I believe, generally admitted that the light which we receive from the clear sky is due in one way or another to small suspended particles which divert the light from its regular course. On this point the experiments of Tyndall with precipitated clouds seem quite decisive. Whenever the particles of the foreign matter are sufficiently fine, the light emitted laterally is blue in colour [now called Tyndall blue], and, in a direction perpendicular to that of the lateral beam, is *completely polarized*. . .

"Having disposed of the polarization, let us now consider how the intensity of the scattered light varies from one part of the spectrum to another, still supposing that all the particles are many times smaller than the wave-length even of violet light. The whole question admits of mathematical treatment; but, before entering upon that, it may be worth while to show how the principal result may be anticipated from a consideration of the *dimensions* of the quantities concerned.

"The object is to compare the intensities of the incident and scattered rays; for these will clearly be proportional. The number (i) expressing the ratio of the two amplitudes is a function of the following quantities:— T , the volume of the disturbing particles; r , the distance of the point under consideration from it; λ , the wave-length; b , the velocity of propagation of light; D and D' , the original and altered densities; of which the first three depended only on space, the fourth on space and time, while the fifth and sixth introduce the conception of mass. Other elements of the problem there are none, except mere numbers and angles, which do not depend on the fundamental measurements of space, time, and mass. Since the ratio i , whose expression we seek, is of no dimensions in mass, it follows at once that D and D' only occur under the form $D:D'$, which is a simple number and may therefore be omitted. It remains to find how i varies with T , r , λ , b .

"Now of these quantities, b is the only one depending on time; and therefore, as i is of no dimensions in time, b cannot occur in its expression. We are left then with T , r , and λ ; and from what we know of the dynamics of the question, we may be sure that i varies directly as T and inversely as r , and must therefore be proportional to $T \div \lambda^2 r$, T being of three dimensions in space. In passing from one part of the spectrum to another, λ is the only quantity which varies, and we have the important law:—

* This work has been done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

¹ Phil. Mag., (4) 41, 107, 274 (1871).

When light is scattered by particles which are very small compared with any of the wave-lengths, the ratio of the amplitudes of the vibrations of the scattered and incident light varies inversely as the square of the wave-length and the intensity of the lights themselves as the inverse fourth power.

"I will now investigate the mathematical expression for the disturbance propagated in any direction from a small particle which a beam of light strikes.

"Let the vibration corresponding to the incident light be expressed by $A \cos (2\pi bt/\lambda)$. The acceleration is

$$- A \left(\frac{2\pi}{\lambda} b \right)^2 \cos \frac{2\pi}{\lambda} bt;$$

so that the force which would have to be applied to the parts where the density is D' , in order that the wave might pass on undisturbed, is per unit of volume,

$$- (D' - D) A \left(\frac{2\pi b}{\lambda} \right)^2 \cos \frac{2\pi}{\lambda} bt.$$

To obtain the total force which must be supposed to act over the space occupied by the particle, the factor T must be introduced. The opposite of this conceived to act at O (the position of the particle) gives the same disturbance in the medium as is actually caused by the presence of the particle. Suppose, now, that the ray is incident along OY , and that the direction of vibration makes an angle α with the axis of x , which is the line of the scattered ray under consideration—a supposition which involves no loss of generality, because of the symmetry which we have shown to exist round the line of action of the force. The question is now entirely reduced to the discovery of the disturbance produced in the aether by a given periodic force acting at a fixed point in it. In his valuable paper 'On the Dynamical Theory of Diffraction,' Professor Stokes¹ has given a complete investigation of this problem; and I might assume the result at once. The method there used is, however, for this particular purpose very indirect, and accordingly I have thought it advisable to give a comparatively short cut to the result, which will be found at the end of the present paper. It is proved that if the total force acting at O in the manner supposed be $F \cos (2\pi bt/\lambda)$, the resulting disturbance in the ray propagated along OX is

$$\zeta = \frac{F \sin \alpha}{4 \pi b^2 D r} \cos \frac{2\pi}{\lambda} (bt - r).$$

Substituting for F its value, we have

$$\zeta = A \frac{D' - D}{D} \cdot \frac{\pi T}{r \lambda^2} \sin \alpha \cos \frac{2\pi}{\lambda} (bt - r),$$

an equation which includes all our previous results and more."

"So much for a single particle. In actual experiments, as for instance with Professor Tyndall's 'clouds', we have to deal with an immense number of such particles; and the question now is to deduce what their effect must be

¹ Cambridge Phil. Trans., 9, 1 (1849).

from the results already obtained. Were the particles absolutely motionless, the partial waves sent out in any direction from them would have permanent relations as to phase, and the total disturbance would have to be found by compounding the *vibrations* due to all the particles. Such a supposition, however, would be very wide of the mark; for, in consequence of the extreme smallness of λ , the slightest motion of any particle will cause an alteration of phase passing through many periods in less time than the eye could appreciate. Our particles are, then, to be treated as so many *unconnected* sources of light; and instead of adding the *vibrations*, we must take the *intensities* represented by their squares. Only in one direction is a different treatment necessary, namely along the course of the primary light. I mention this because it would not otherwise appear how the reduction in the intensity of the transmitted light is effected; but we do not require to follow the details of the process, because when once we know the intensity of the light emitted laterally, the principle of energy will tell us what the primary wave has lost.

"The intensity of the light scattered from a cloud is thus equal to

$$A^2 \frac{(D' - D)^2}{D^2} \sin^2 \alpha \propto \frac{\pi^2 \Sigma T^2}{\lambda^4 r^2}.$$

where ΣT^2 is the sum of all the squares of T . If T^2 be understood to denote the mean square of T (*not* the square of the mean value of T), and m the number of particles, $\Sigma T^2 = m T^2$. If the primary light be unpolarized, the intensity in a direction making an angle β with its course becomes

$$A = \frac{(D' - D)^2}{D^2} (1 + \cos^2 \beta) \frac{m \pi T^2}{\lambda^4 D^2}.$$

"The principle of energy makes it clear that the light emitted laterally is not a new creation, but only diverted from the main stream. If T represents the intensity of the primary light after traversing a thickness x of the turbid medium, we have $dT = -kT\lambda^{-4} \frac{dx}{k\lambda^{-4}x}$ where k is a constant independent of λ . On integration, $I = I_0 \epsilon$, if I_0 correspond to $x = 0$, — a law altogether similar to that of absorption, and showing how the light tends to become yellow and finally red as the thickness of the medium increases."

These equations show that the light scattered at right angles is always richer in the shorter wave-lengths, while the transmitted light is always richer in the longer wave-lengths. For very fine particles the scattered light will be a violet-blue changing to blue as the particles get larger. When the particles are no longer small relatively to the wave-length, ordinary reflection will come in and there may be enough white light to mask the blue. The Rayleigh theory has stood the test of experiment for over sixty years, which is doing well and which is extraordinary in view of the fact that data were published forty years ago which were sufficient, had people paid attention to them, to have proved that the Rayleigh theory cannot be adequate.

In 1892 Aitken¹ published his study of the transmitted colors in the case of condensation, using both a steam jet and an expansion apparatus. "As has

¹ Proc. Roy. Soc., 51, 408 (1892).

been stated, a slight expansion produces a blue colour if the number of particles be small, and if the expansion be increased after the blue is produced, the colour changes; and we shall now describe the successive colours, which appear as the degree of expansion is increased, that is, as the size of the water particles is increased. When the expansion begins, blue is the first distinct colour to appear; but very pale yellow and slightly reddish colours have been noticed before the expansion was sufficient to produce the blue. These reddish colours can be seen very distinctly when we use an excessively great number of particles, and they are best seen with gas light. These reddish colours change imperceptibly into blue as the expansion is increased, and the blue in turn changes by minute degrees into green with further expansion, and the green in turn changes to yellow; then a brownish colour appears which changes to a somewhat mixed purple; then the blue returns again, to be followed by green and yellow as the expansion is still further increased. It is not easy to get this sequence of colours carried so far. Sometimes one stroke of the pump only carries the colour on to yellow; sometimes it may go to the second blue or green, but less frequently to the second yellow. The final colour depends on the number of particles present. It is necessary to have a good many drops, so that the colour may be distinct, and yet not too many, or the expansion may not be sufficient to grow the particles large enough to give the second series of colours. It is found that a high expansion, produced by two or more strokes of the pump, does not give satisfactory results.

"To observe the effect of temperature on these colour phenomena, another tube was prepared with glass ends and jacketed, so that the air in it might be heated or cooled to any desired temperature. The result was very much what might have been expected: at the different temperatures all the colours made their appearance in the usual order; but there was a considerable difference in the amount of expansion required to produce a given colour with change of temperature. At a high temperature each of the colours appeared with a less expansion than the temperature was low. [This means that at the higher temperature a given expansion produces larger drops.] In making these tests the number of dust particles in the air must be kept as constant as possible. For this purpose windows and doors should be kept closed for some time before beginning, and the experiments should be repeated without change of conditions. When the air was cooled to about 35° , it took two strokes of the pump to develop a full blue, and three strokes made it only green. At a temperature a little over 50° , two strokes made it green, while if the air was heated to about 80° , two strokes sent it past blue and green and on to yellow, and less than one stroke made it full blue. These differences are due to more vapour being present and being condensed, with the same amount of expansion, when the air is hot than when it is cold. It should be stated that in all cases the air was saturated, the inside of the tube being wet."

"These experiments show that the colour produced by the small drops of water depends on the size of the drops, and the depth of the colour on their number. But it is not so easy to follow the manner in which the drops produce the colour. If we take the simplest case, we can easily see how part, at

least, of the colour is produced. In the steam jet condensing dense, and colouring the transmitted light yellow, part of the effect is no doubt due to some of the particles in that form of condensation being so small that they reflect and scatter the shorter waves of light, while they allow the longer ones to pass through. The colour in this case is partly caused in the same way as the yellow produced by small particles suspended in liquids, as in Brücke's experiments with mastic, or as when silver chloride is formed from a solution of the nitrate. The light reflected by the liquids in these experiments is of a bluish tint, complementary to the yellow light transmitted by them, and this blue light is polarised. It has been found that, when the steam jet is of a good yellow by transmitted light it reflects a good deal of a bluish light; and further, this blue light is polarised in the same way as the light from the small particles in the experiments with liquids.

"While this explanation helps us to understand the manner in which the yellow light is produced in the steam jets, yet it fails to explain the succession of colours seen in the expansion experiments, where blue first appears, then green and yellow; and when the expansion is still further increased, the blue again returns to give place to a second green and yellow. The most probable explanation of these colour phenomena is that they are produced in the same way as the colours in plates, somewhat after the manner Newton thought the colour of the sky was produced. The order of succession of the colours in thin plates is the same as in these condensation phenomena. As no white follows the first blue, it seems probable that the first spectrum, or order of colours, is not observed; that the two generally seen are the second and third."

With increasing size of drops the transmitted colors apparently vary: yellow, red, blue, green, yellow, brown, purple, blue, green, yellow. This would be quite regular if the brown had been a red. Regardless of that, there are certainly two blues and apparently three yellows, a result that cannot possibly be deduced from Rayleigh's equations. Five years earlier R. von Helmholtz¹ reported that the light scattered by a steam jet varied with increasing size of drops: blue, whitish, purple, red, yellow, green, pale blue. These studies were carried much farther by Barus² whose data are given in Table I.

At the time, Barus said that "there can be no doubt that the succession of the colors of cloudy condensation is identical with the corresponding succession in Newton's rings of the first and second order, seen by transmitted light under normal incidence."

In 1902 Barus³ said: "It may be noted that the order of size of particle is about ten times longer than would follow if the same (axial) colour were produced by interference in thin plates. . . . The axial colours vanish completely (become white) before even one half of the coronas have been passed. Experiment shows, therefore, conformably with the given interpretation that the condition of optical saturation (removal of the original white light) is a line of vision quite blocked by water particles all of rigorously the same size.

¹ Wied. Ann., 32, 1 (1887).

² Am. Meteorol. J., 9, 488 (1893).

³ Phil. Mag., (6) 4, 24 (1902).

TABLE I
Transmitted Colors of Drops of Water

Color of jets	Interference colors	Thickness of air plate, μ
White.....	White	0.02
Yellow.....	Yellow white	0.048
	Brown white	0.079
Orange.....	Yellow brown	0.109
Brown.....	Brown	0.117
Opaque.....	Red	0.129
Opaque.....	Carmine	0.133
Opaque.....	Dark-red brown	0.137
Dark violet.....	Dark violet	0.140
Indigo.....	Indigo	0.153
Blue.....	Blue	0.166
Gray blue.....	Gray blue	0.215
Blue green.....	Blue green	0.252
Green.....	Pale green	0.268
	Yellow green	0.275
Green yellow.....	Yellow green	0.282
	Green yellow	0.287
Straw yellow.....	Yellow	0.294
	Orange	0.332
Muddy brown.....	Brown orange	0.364
	Light carmine	0.374
Pale purple.....	Purple	0.413
Pale violet purple.....	Violet purple	0.421
Pale violet.....	Violet	0.433
Pale indigo.....	Indigo	0.455
	Dark blue	0.474
Faint green.....	Green blue	0.499
	Green	0.550
Faint yellow green.....	Yellow green	0.554
	Dull yellow	0.575

Thus it would seem as if each single water particle colours the area of its projection.

"Now what kind of absorption is this which occurs for particles of such surprisingly large dimensions relatively to the wave-length of light, which occurs moreover in just as marked a degree if the particles are electrical insulators like the precipitates from benzine and petroleum vapours? For though one cannot regard a water particle captured by a saline nucleus as quite an insulator, there seems to be no electrical conduction possible for the case where a sulphur nucleus condenses benzine vapour." In a later paper Barus¹ revises his figures a little and gets value of 6-9 for the ratio d/D , where d is the diameter of the fog particles and D the thickness of an air plate

¹ Am. J. Sci., (4) 25, 224 (1908).

giving like interference colors. "From this it appears that the strong axial blues of the first order must belong to particles even larger than 0.0001 cm [$> 1\mu$] in diameter, and that all particles are more than six times larger than would be demanded for interference.

"Recently I have considered the case of a lamellar grating, in which diffractions are obtained from a uniform succession of alternately different thicknesses of clear glass. Experiments with such gratings were originally made by Quincke and there is a full theoretical treatment by Verdet. The behavior of this grating differs from that of the usual kind in the occurrence of an additional factor

$$\cos^2 (\pi d(n - 1) + \pi a \sin \delta) / A$$

where n is the index of refraction, d the difference in thickness between thin strips of width a and of thick strips of width b , δ the angle of diffraction. Hence for axial color, $\delta = 0$, minima occur at $(n - 1)d = (2m + 1)\lambda/2$, whereas for Newton interferences the minima occur for a thickness of D in case of transmitted light, where $2\mu D = (2m + 1)\lambda/2$; whence $d/D = 2n/(n - 1)$. In case of water $n = 1.33$ or $d/D = 8.0$. This result, holding for a grating of transparent strips, is so near the above datum $d/D76$ for a medium of transparent particles (for which there is no theory), that it seems reasonable to conclude that the actual colors are referable to the same type of phenomenon in both cases. The need of observations through long columns in case of fog particles suspended in air is additionally confirmative, since the contribution of color due to one particle must be exceedingly small."

Similar phenomena have been observed in every-day life. Piazzzi Smyth¹ reports that for several days in India the disk of the sun appeared blue or green in the morning and evening. Aitken² considers this as due to the presence of drops of water of the right size. He reports that Principal Forbes observed colors in the steam escaping from a safety valve and Mr. Lockyer,³ when on Windermere, saw the sun of a vivid green through the steam of a little paddle-wheel steamer. Whympers⁴ saw a green sun through volcanic dust from Cotopaxi. Blanc⁵ showed that a ripened photographic emulsion transmits a blue image of the sun. Keen and Porter⁶ have shown that very fine particles of colloidal sulphur scatter blue and transmit red preponderantly, just as they should; but they transmit blue at some stage in the agglomeration. The explanation offered by Raman and Ray⁷ accounts for the decreased opacity but not for the blue color. Wolfgang Ostwald and Auerbach⁸ have found a color series for sulphur of blue, green, yellow, orange, red, violet, blue, which is perfectly satisfactory except that they consider the first two colors as due to sulphur in true solution. This is probably an error.

¹ Trans. Roy. Soc. Edinburgh, **32**, 389 (1884).

² "Collected Scientific Papers," 270 (1923).

³ Nature, **28**, 155 (1883).

⁴ Travels among the Great Andes of the Equator," 324 (1892).

⁵ Bull. Soc. franç. Photographie, (2) **17**, 256 (1911).

⁶ Proc. Roy. Soc., **89A**, 370; Rayleigh: **90A**, 219 (1916); Auerbach: Kolloid-Z., **27**, 223 (1920).

⁷ Proc. Roy. Soc., **100A**, 102 (1921).

⁸ Kolloidchem. Beihefte, **30**, 336 (1926).

Harrison¹ explains the colors of the starch-iodide complex as a phenomenon of dispersion, meaning scattering. "An alcoholic suspension of starch is mixed with an alcoholic solution of iodine until there is a distinct yellow color. On adding water the color changes to orange, red, and violet, becoming blue on extreme dilution. On adding alcohol to a blue solution of starch and iodine the color changes reverse, winding up with a yellow." This is a very important experimental observation; but it is not clear whether it is the starch or the iodine that is being dispersed.

We have checked up on some of the points involved. When an equal volume of 0.106 M HCl is added to a 0.051 M sodium thiosulphate solution, the mixture goes through the following color changes when viewed by transmitted light. Almost immediately it becomes a pale yellow, turning to orange, which changes to red in about thirty minutes and then becomes purplish. By this time the solution has become decidedly opaque. At the end of an hour the solution is too opaque to transmit light appreciably from an incandescent lamp or even from the sun. After about eighty minutes the solution begins to clear to a beautiful blue solution showing almost no sign of turbidity. This blue persists from one hour to six hours, the time varying with the preparation. Sometimes the solution shows no more color changes, the sulphur settling out gradually and leaving the supernatant liquid clear and colorless. If one is lucky however, the color changes from blue to greenish-blue, green, or lavender. In all cases the sulphur has settled and the solution has become colorless at the end of sixteen to twenty-four hours. More dilute solutions show about the same changes of color; but the color is less intense.

The best effect is produced when the source of light is distant and fairly well circumscribed, such as the sun or a distant window. Although electric light filaments do very well (they alone being colored), a point source is neither necessary nor desirable if a larger source is available. When the solution is diluted with water at any color stage, the color changes in intensity only, becoming paler. This indicates that the distance between the particles is not a factor in producing the color. Our results confirm those of Aitken and of Barus.

Special titration experiments showed that the sulphur is precipitated practically completely at the start and that the increase in size of the particles must therefore be accompanied by a corresponding decrease in the number. The reflected colors in these preparations are always complementary to the transmitted colors, as is shown in Table II in which is recorded a run that went faster than usual.

When examined under the microscope the sulphur particles are seen as perfect spheres. The particles in the solutions transmitting yellow are about 0.2μ in diameter. They are about 0.5μ in the red solutions, $1-2\mu$ in the blue solutions, and $3-4\mu$ in the green solutions.

There is some evidence that the color varies with the refractive index of the medium, smaller particles giving a blue when the index of refraction is less. A corollary of this is that, in a medium with a higher refractive index than

¹ Kolloid-Z., 9, 5 (1911).

TABLE II
Colors of Sulphur Sols

Min.	Transmitted	Reflected
1	Yellow	Blue
2	Orange	Blue
3	Deep orange	Blue
4	Red	Greenish blue
7	Deep red (opaque)	Greenish blue
9	Purple	?
10-15	Bluish purple	Yellowish red
20	Deep blue	Orange red
25	Greenish blue	Orange red
30	Green	Red
35	Light green	Pink

water, the transmitted light should be displaced toward the red. This was found to be the case. The thiosulphate solution was prepared in one percent agar and a layer 1 mm thick was allowed to set to a jelly. This layer was immersed in a hydrochloric acid solution and it then passed through the usual color changes, though relatively slowly. When the blue stage was reached the film was removed, washed and allowed to dry. It was then a dirty red by transmitted light. Addition of a drop of water to any part of the film produced a deep blue spot, the red color reappearing on drying. This could be repeated at will. The dried film was then shaved down with a razor blade until the microscope showed only a single layer of sulphur particles present. The color was still red, though not so intense.

Films of a one percent agar jelly containing sodium thiosulphate were made about 0.5 mm thick and were covered with rectangular pieces of glass. They were allowed to stand for twenty-four hours in a hydrochloric acid solution. A gradation of colors was obtained with red at the edges and blue towards the center of the film. In addition there could be seen a well-defined repetition of the colors, so that within the width of 1 cm in some slides as many as three complete color series could be seen, each ranging from yellow to green. A clear space was left in the middle of the film about 0.5 cm wide. When these jelly preparations were kept moist, they retained their colors for about a month.

The following variation produced sulphur films showing reds and blues which are permanent. A layer of jelly ten centimeters square and about 1 mm thick on a glass plate was covered with another glass plate supported at the corners by thin pieces of cork and immersed in hydrochloric acid solution for twenty-four hours in the usual way. The cover plate was removed carefully. When the film was washed and allowed to dry, portions of it showed a beautiful transmitted blue. The colors in this case are best seen by means of a frosted electric light bulb. The blues must originate with some color in the higher series. When the refractive index of agar is increased by drying a lower order blue is observed.

A similar agar jelly in test tubes, overlaid with a hydrochloric acid solution, gives beautifully colored rings, simulating Liesegang rings and changing from reds to blues and greens as one looks through different portions of the tube. These jelly cylinders can be slipped out of the tubes and slices cut out at the differently colored layers. A cube of green jelly was cut out and allowed to soak in glycerine until all the water was displaced. The jelly turned blue. On replacing it in water so that the glycerine was displaced, the jelly turned green again.

When slices of blue and green jelly were allowed to dry, they turned various shades of orange and red. Wetting the layers restored the original colors. When examined under the microscope the sulphur particles appeared as perfect spheres with light centers. They were closely surrounded by a thin colored ring which was the same color as that of the entire mass. This makes it clear why the distance between the particles affects only the depth of color and not the hue.

Dry films of sulphur which show good transmitted blues can be obtained by subliming the sulphur on glass. Barium sulphate can be precipitated on glass so as to transmit blue. When these were painted with collodion, they turned red when still wet. An emulsion of lanolin in water showed a transmitted red when squeezed between glass plates. If the film is heated carefully the transmitted light changes to blue. When more pressure was put on the plates the red color returned.

TABLE III
Transmitted Colors of Different Sols

Substance	Color	Particle Size	Refracture Index
Sulphur	Red	0.5μ	1.93
	Blue	$1-2\mu$	
	Green	$3-4\mu$	
Zinc oxide	Red	$0.1-0.15\mu$	2.03
	Purple	$0.5-1\mu$	
Silver bromide	Red	0.1μ	2.25
	Green	0.5μ	
Copper oxide	Red	$0.1-0.5\mu$	2.70
	Blue	$1-2\mu$	
Carbon black	Red	$0.1-0.5\mu$	2.42
	Blue	1μ	
Selenium	Blue	0.5μ	2.9
Silver	Yellow	0.09μ	0.16
	Violet	0.15μ	
	Blue-green	0.18μ	
Gold	Red	$0.01-0.04\mu$	0.37
	Blue	0.08μ	
Copper	Red	$<0.1\mu$	0.64

Experiments were made with various suspensions in water to determine approximately the relation between color and particle size. The color data given in Table III refer to transmitted light.

The values for transmitted blue are not very different for sulphur, zinc oxide, copper oxide, and carbon black. They agree well with the values found by Barus for water, which indicates that the refractive index of the particles has relatively little effect on the color. The values for silver bromide and for selenium are lower. No explanation of this will be attempted at present. With silver, copper and gold the blue occurs at a very much smaller diameter than in the case of the other substances. Two characteristics of these three metals are great opacity and abnormally low apparent indices of refraction. For the time being, we are laying more stress on the opacity than on the apparent indices of refraction.

There is still no theory of the phenomena and apparently no question as to the phenomena. We have tried for six years to get physicists interested in the problem, but in vain. It is not a fashionable problem at the present time. We, of course, do not know enough about the mathematical theory of light to solve the problem ourselves and it therefore seems wise to formulate the problem now as we see it in the hope that some day some physicist will clean up the whole thing.

Since Rayleigh's theory describes the facts pretty well over a certain range and since it does not account for the periodicity which has been shown to occur, it is pretty clear that the real formulation, when it comes, must take account of the recurrent nature of the phenomena and must reduce to something equivalent to the Rayleigh formula over a certain range of diameters. Pending the discovery of such an equation, let us consider only three colors for the moment and let us make the empirical assumption that with increasing size of particle the colors by transmitted light change yellow, red, blue, yellow, red, blue, yellow, red, blue, indefinitely until some other factor becomes predominant. All color due to scattering disappears when the suspended particles become small enough. When the particles become sufficiently large, we get the ordinary phenomena of reflection and refraction. We will make the additional, plausible assumption that the disappearance of all color due to suspended particles occurs at smaller diameters the more opaque the particle is.

On this basis the colors of colloidal gold and colloidal silver are similar in nature to the colors of the steam jets studied by R. von Helmholtz, Aitken, and Barus among others. The difference is merely that we are dealing with a different cycle in the cases of the metals. If this is true, particles of silver of the general order of $1-2\mu$ in diameter should transmit blue light. These would not stay up in water; but the experiment could be tried in an agar or gelatine jelly. A necessary consequence of the general hypothesis is that it should be possible to prepare yellow, red, and blue sols of any metal whatsoever, provided it is stable in the medium. This seems to be true in general, though there are some gaps in our knowledge and there may be other factors coming in.

Yellow, red and blue sols of silver, mercury, gold, copper and selenium have been reported, though the yellow sols of gold and copper and the blue

sols of selenium are not easy to make. Yellow and red sols of platinum are known. Probably a complete set could be prepared if necessary. Sodium fogs transmit yellow, a color which the vapor absorbs. Sodium and potassium salts may be colored blue by cathode rays.

Wolfgang Ostwald¹ points out that "with all the colloids studied—and therefore probably according to some law—the maximum absorption is displaced with increasing dispersity of the colloid towards the region of shorter wave-lengths." He illustrates this by the case of gold, for which the transmitted light varies with decreasing dispersity of the gold in the order: yellow, orange, red, violet, blue, green. Ostwald has ignored the cyclic nature of the phenomenon although he is familiar with the work of Barus. Ostwald² puts gold sols and drops of water in two different categories, which seems unwise.

The experiments of Kirchner and Zsigmondy³ on colloidal gold in gelatine agree with those of Faraday⁴ but do not agree with our experiments on sulphur in agar. Some of the gold sols changed from red to blue on drying and went back to red when moistened. The sulphur jellies went from blue to red on drying and back to blue when moistened. A special investigation will be necessary in order to account for the apparent discrepancy. Kirchner explained the color change on the basis of Planck's dispersion theory for isotropic dielectrics. He regarded the particles as resonators, which behaved differently when in close proximity. This cannot be true because all experiments show that the distance between the particles affects only the intensity of the color.

Mulliken⁵ reports that cholesterin benzoate crystallizes in pearly white leaflets which fuse to a turbid liquid at 145.5° (uncorrected). At 178.5° (uncorrected) the turbidity suddenly disappears. In cooling, a brilliant display of opalescent colors is exhibited, among which a brilliant blue, appearing at about the temperature of the higher melting point, followed by a violet-blue just before complete solidification, are the most prominent. The colors disappear very quickly." It was hoped that these colors might be due to scattered light of the type that we have been considering; but this is not the case.

When cholesterin benzoate is fused and allowed to cool, it goes through a series of beautiful iridescent colors which disappear when the compound has finally solidified. The iridescence is due to the formation of liquid crystals which form on cooling and which give brilliant polarization colors under the microscope. We are apparently dealing with the Christiansen affect. Cholesterin acetate gives less marked color changes than the benzoate; but a 1:1 mixture of the two gives iridescent colors on cooling from the melt which are much more brilliant than those from the benzoate alone. A eutectic mixture is formed which melts at a much lower temperature than either of the components.

¹ Kolloidchem. Beihefte, 2, 409 (1911).

² "Licht und Farbe in Kolloiden," 347, 427 (1924).

³ Ann. Physik, (4) 15, 573 (1904).

⁴ Phil. Trans., 147, 175 (1857).

⁵ "A Method for the Identification of Pure Organic Compounds," 1, 172 (1904).

The general results of this paper are as follows:—

1. With drops of water the colors by transmitted light change periodically with varying size of the drops.
2. A transmitted blue is obtained when the diameters are $1-2\mu$.
3. A similar blue is obtained with many solids at approximately the same diameters.
4. The colors of such particles do not seem to vary appreciably with the indices of refraction of the particles but do vary considerably with changing index of refraction of the surrounding medium.
5. The color changes with changing particle sizes show an astonishing parallelism with interference colors.
6. It is not known whether an adsorbed film takes part in the production of the colors.
7. The colors of the colloidal metals do not depend primarily on the nature of the metal. It is probable that one can make yellow, red, and blue sols of any metal.
8. The colors of colloidal metals seem to be identical in nature with the colors of particles of water or sulphur, but can occur at much smaller diameters.
9. It is probable that the colors of colloidal metals represent another cycle in the water series, made possible by the extreme opacity of the metallic particles.
10. Since the Rayleigh equations for the scattering of light by particles small relatively to the wave-lengths of light do not account for the periodic changes which actually occur, the Rayleigh equations cannot be an accurate statement of things as they are.
11. Since the Rayleigh equations do describe the facts very well over a limited range of diameters, it is probable that the true equations will become practically equivalent to the Rayleigh equations for the same range of particle sizes.
12. The effect of drying gold sols in gelatine is apparently different from the effect of drying sulphur sols suspended in agar. Special experiments are called for to determine whether the discrepancy is due to the difference between gold and sulphur, is due to the difference between gelatine and agar, or is due to experimental error.

Cornell University.

NITROGEN COMPOUNDS OF GALLIUM

I. The Ammonates of Gallium Tribromide and Gallium Triiodide

II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia*

BY WARREN C. JOHNSON AND JAMES B. PARSONS

The halides of the elements of the third group, namely, boron, aluminium, gallium, indium and thallium, appear to show divergent properties in their behavior toward ammonia. In general, the halide reacts with ammonia gas or liquid ammonia to form an addition compound (ammonate). As an alternative, the halide may be partially or completely ammonolyzed with the formation of the ammonium salt of the halogen and the amide or imide of the metal. Whether or not the ammonolytic reaction will proceed is dependent in a large measure upon the nature of the cation in combination with the halogen.

Boron trifluoride¹ combines with one molecule of ammonia to form an ammonate which has recently been shown to be appreciably ammonolyzed² in liquid ammonia solution. The trichloride,³ tribromide⁴ and triiodide⁵ of boron form ammonates with ammonia at low temperatures but readily undergo ammonolysis at slightly elevated temperatures. All the halides of aluminum^{6,7,8} form ammonates with no indication of ammonolysis. The corresponding salts of indium⁹ and thallium,¹⁰ with the exception of the fluorides, behave similarly.

Gallium occupies an intermediate position in the third group of elements. Since it is more electropositive in nature than aluminium, one would predict its salts to be stable in liquid ammonia, particularly at low temperatures. The following work was undertaken to determine some of the properties of the halides of gallium in liquid ammonia solution.

[Experimental

The halides of gallium were prepared by the direct combination of the elements according to a previously described method.¹¹ The tribromide and triiodide of gallium were selected since appreciable quantities of these salts were available. Liquid ammonia, dried over sodium in small steel cylinders, was employed in all experiments.

* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

¹ Mixer: *Am. Chem. J.*, **2**, 153 (1880).

² Kraus and Brown: *J. Am. Chem. Soc.*, **51**, 2690 (1929).

³ Joannis: *Compt. rend.*, **135**, 1106 (1902).

⁴ Besson: *Compt. rend.*, **112**, 1002; **113**, 78 (1891); *Stock: Ber.*, **34**, 949 (1901).

⁵ Besson: *loc. cit.*; Joannis: *loc. cit.*

⁶ Clark: *Am. J. Sci.*, (5) **7**, 1 (1924).

⁷ Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," **5**, 319-20, 326 (1924).

⁸ Franklin: *J. Am. Chem. Soc.*, **27**, 847 (1905).

⁹ Klemm: *Z. anorg. Chem.*, **163**, 240 (1927).

¹⁰ Biltz and Stollenwerk: *Z. anorg. Chem.*, **119**, 97 (1921).

¹¹ Johnson and Parsons: *J. Phys. Chem.*, **34**, 1210 (1930).

Gallium Tribromide Hexammonate.

Dry ammonia gas was condensed at -33.5° on gallium tribromide in a tube which could be readily detached from a "vacuum line" and weighed. The usual technique was employed to prevent contact of the salt with air and moisture. Reaction followed immediately after the introduction of ammonia to produce a white powder which appeared to be only slightly soluble in liquid ammonia. After the mixture had been allowed to stand in contact with the ammonia for several hours, the excess ammonia was allowed to escape and the system was thoroughly evacuated. The tube and contents finally assumed a constant weight at room temperature. The following results were obtained for two different preparations.

TABLE I

The Formation of Gallium Tribromide Hexammonate

Weight of GaBr ₃ grams	Weight of ammonia reacted (grams)	Ratio NH ₃ /GaBr ₃ found
0.4865	0.1632	6.09
0.4690	0.1533	5.94

Although ammonia was removed from the compound in vacuo until the weight of the tube and contents assumed a constant value and the pressure was reduced to 10^{-4} mm., its odor could be detected when the ammonate was exposed to air. A sample of the material after exposure to air, was analyzed for ammonia by distillation from an alkaline solution into standard acid solution, and for bromine by the usual procedure. The ammonia content was found to correspond to approximately two-thirds of the total amount that had reacted with the gallium tribromide, while the bromine analysis agreed well with the calculated value.

Anal. Subst., 0.0553; NH₃, 0.0099; AgBr, 0.0756. Calcd. for GaBr₃.6NH₃, NH₃, 24.82; Br, 58.24. Found: 17.94, 58.17.

These facts indicate that while ammonia is lost on exposure of the ammonate to air, water replaces the ammonia so that the net change in weight is very small. However, this process was found to be readily reversible. When the material was again subjected to liquid ammonia and the excess ammonia removed as described above, analysis showed six molecules of ammonia to be in combination with the gallium tribromide.

In order to obtain pure samples of the ammonate for analysis, they were sealed off in small tubes attached to the reaction tube without exposure to the air. The tubes were then cracked with a piece of hot glass and finally broken in a Kjeldahl flask under the alkali solution. The results recorded below were obtained on two samples of the ammonate; sample I was exposed to air and then treated with liquid ammonia to restore the ammonate to its original condition, while sample II was prepared and manipulated in the absence of air and moisture.

Anal. Subst., I, 0.1062, II, 0.6221; NH₃, 0.0263, 0.1531. Calcd. for GaBr₃.6NH₃, NH₃, 24.82. Found: 24.74, 24.62.

Sample I was analyzed for bromine by the usual method.

Anal. Subst., 0.1062; AgBr, 0.1453. Calcd. for $\text{GaBr}_3 \cdot 6\text{NH}_3$; Br, 58.24; Found: 58.22.

While the above values show the quantity of ammonia absorbed in the reaction, they do not indicate the nature or mechanism of the process. There are two possibilities:

- (1) $\text{GaBr}_3 + 6 \text{NH}_3 = \text{GaBr}_3 \cdot 6\text{NH}_3$ (addition or ammonation).
- (2) $\text{GaBr}_3 + 6 \text{NH}_3 = \text{Ga}(\text{NH}_2)_3 + 3 \text{NH}_4\text{Br}$ (ammonolysis).

If ammonolysis were to take place, the ammonium bromide, which is highly soluble in liquid ammonia, could be readily separated from the slightly soluble product of the reaction (presumably the amide or imide of gallium). Attempts to carry out such a separation were made as follows: a Pyrex tube about 1.5 cm. in diameter and 15 cm. in length was fitted with a side arm stopcock and a second leg of the same dimensions. A small amount of gallium tribromide was placed in the tube which was then sealed off and evacuated. Ammonia was condensed on the salt and the system was allowed to stand for several hours. The clear solution above the salt was carefully decanted into the second leg of the tube. A Dewar flask of ammonia was placed about the main portion of the tube and the ammonia distilled out of the leg to the original sample with the deposition of any material that may have dissolved. Ten such extractions were made until a quantity of the soluble portion sufficient for an analysis was obtained. An examination of this material proved it to be identical with gallium tribromide hexammonate. This experiment shows that ammonolysis does not take place and that the solvated salt is slightly soluble in liquid ammonia.

Additional proof for this result is based upon the fact that ammonium bromide is an acid in liquid ammonia and, when treated with a strongly electro-positive metal such as sodium, liberates hydrogen according to the following equation:



Experiments showed, however, no indication of hydrogen gas when metallic sodium was added to a solution of gallium bromide in liquid ammonia. On the other hand, reduction of the salt to metallic gallium appeared to take place. According to the results of these experiments it is concluded that an ammonate, $\text{GaBr}_3 \cdot 6\text{NH}_3$, is formed when gallium tribromide is subjected to liquid ammonia.

Properties. The ammonate is obtained as a white powder from liquid ammonia solution. In the absence of moisture it is remarkably stable. In moist air, water molecules replace the ammonia which is readily liberated as a gas. This process is found to be reversible; in other words, ammonia will replace the water in liquid ammonia solution. Dry air does not appear to have any effect upon the ammonate. It is easily soluble in alkali and hydrochloric acid solutions. At higher temperatures, about 100°C, the ammonate slowly loses ammonia when subjected to a high vacuum. The ammonate exhibits an appreciable solubility in liquid ammonia.

Gallium Triiodide Hexammonate.

Gallium triiodide was treated with liquid ammonia in a manner analogous to that employed in the bromide investigation described above. A reaction was found to proceed rapidly with the formation of gallium triiodide hexammonate as is indicated by the following results:

TABLE II

The Formation of Gallium Triiodide Hexammonate

Weight of GaI ₃ , g.	Weight of ammonia reacted, g.	Ratio NH ₃ /GaI ₃ found
0.8728	0.1981	6.00
0.5087	0.1142	5.94

When the ammonate was exposed to air, ammonia was liberated but was found to be restored as in the case of the bromide by a second treatment with liquid ammonia. The product exposed to air was analyzed for ammonia:

Anal. Subst., 0.3351. NH₃, 0.0549. Calcd. for GaI₃.6NH₃; NH₃, 18.49. Found: 16.39.

Another portion of the product exposed to air was restored to its original condition in liquid ammonia, the ammonate was freed of the excess ammonia and finally analyzed.

Anal. Subst., 0.2430; NH₃, 0.0453. Calcd. for GaI₃.6NH₃; NH₃, 18.49. Found: 18.64.

A third sample was prepared and analyzed in the absence of air and moisture.

Anal. Subst., 0.6246; NH₃, 0.1159. Calcd. for GaI₃.6NH₃; NH₃, 18.49. Found: 18.55.

Analyses were not made here for gallium and iodine since the samples of the triiodide were taken from a larger lot which had been carefully purified and analyzed (see ref. 11).

The increase in weight, as given in Table II, and the ammonia analyses show six molecules of ammonia in combination with one gram molecule of gallium triiodide. The ammonate was found to possess properties similar to those of the corresponding bromide salt.

II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia

The third group elements boron, aluminium, indium and thallium are known in combination with fluorine. According to the literature, no attempts have been made to study the reactions of gallium with fluorine and fluorides. The present authors¹¹ observed that metallic gallium reacts readily with hydrofluoric acid (50% solution) to produce a white substance, insoluble in excess acid and of much greater volume than the original amount of metal. In the present investigation, this reaction has been studied in more detail to show that the product is a hydrated fluoride of gallium, GaF₃.3H₂O. This hydrated salt is also studied in the liquid ammonia solution.

Gallium Trifluoride Trihydrate.

The hydrated salt was prepared by two methods, namely, (A) by a reaction of metallic gallium with hydrofluoric acid (50% solution) and (B) by a reaction between gallic oxide and hydrofluoric acid (50% solution).

(A). A small amount of metallic gallium was treated with hydrofluoric acid in a platinum crucible. Reaction followed immediately to produce a white substance which appeared to be insoluble in the acid. The reaction was hastened considerably by making contact between the metallic gallium and the crucible with a piece of platinum wire. After the reaction was allowed to proceed in this manner for several hours, the excess acid was removed by evaporation over a steam bath. The increase in weight of the product over that of the metal suggests the formation of $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ as is shown in the following table.

In each case the actual yield of the product was slightly less than that calculated for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$. It was noticed, however, that during the reaction and the evaporation of the excess acid, a small amount of the solution was carried out of the crucible in the spray of escaping hydrogen and hydrogen fluoride.

TABLE III

Preparation of Gallium Trifluoride Trihydrate

Weight of gallium, grams	Weight of salt obtained, grams	Weight calc. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$.
0.4858	1.2347	1.2590
0.8155	2.0644	2.1149
0.5418	1.3933	1.4055

Analysis. Two samples of the salt, each from a different preparation, were analyzed for gallium and fluorine. For the gallium analysis, the salt was dissolved in dilute hydrochloric acid, gallium hydroxide was precipitated with ammonium acid sulfite,¹² and the hydroxide was ignited and finally weighed as gallic oxide.

Anal. Subst., 0.2239, 0.2959; Ga_2O_3 , 0.1160, 0.1539. Calcd. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$; Ga, 38.57. Found: 38.54, 38.69.

For the fluorine analysis, the method of Starck and Thorin¹³ was used with slight modification.¹⁴ The fluorine was precipitated as calcium fluoride which was found to be exceedingly difficult to filter on account of its gelatinous structure. Accordingly, the calcium fluoride was precipitated and weighed with a known amount of calcium oxalate. A weighed quantity of sodium oxalate was added to the solution slightly acidified with acetic acid; to this solution was added an excess of calcium chloride. The precipitate was dried at 210° and the weight of calcium oxalate was deducted to give that of the calcium fluoride.

Anal. Subst., 0.3325, 0.2269; CaF_2 , 0.2152, 0.1483. Calcd. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$; F, 31.53. Found: 31.51, 31.82.

¹² Porter and Browning: J. Am. Chem. Soc., **41**, 1491 (1919).

¹³ Starck and Thorin: Z. anal. Chem., **51**, 14 (1912).

¹⁴ Sodium oxalate was substituted for oxalic acid.

(B). A more convenient method of preparation of the hydrated fluoride was found in the treatment of gallic oxide with hydrofluoric acid (50% solution).¹⁵ The oxide is readily soluble in this acid solution. When the excess acid is removed by evaporation, $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ is obtained as a fine white powder. The results of this reaction are given in Table IV; the analyses are recorded below.

TABLE IV

Preparation of Gallium Trifluoride Trihydrate

Weight of Ga_2O_3 , grams	Weight of salt obtained, grams	Weight calc. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$, gram
0.1986	0.3756	0.3829
0.4019	0.7728	0.7749
0.3066	0.5875	0.5912

Anal. Subst., 0.5875, 0.5799. Ga_2O_3 , 0.3066, 0.3003. Calcd. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$; Ga, 38.57. Found: 38.83, 38.53.

Properties. Gallium trifluoride trihydrate is a fine white powder as prepared by the above described methods, insoluble in cold water but appreciably soluble in hot water. It is readily soluble in dilute hydrochloric acid and sparingly soluble in hydrofluoric acid (50% solution). It is stable in air; a sample exposed to the atmosphere for several weeks showed no change in appearance or weight. When heated to 140° in a vacuum under the influence of an oil pump and Hg-vapor pump, water is slowly liberated. One-half of the water (1.5 mols) appears to be liberated much more easily than the remaining water molecules.¹⁶

The Action of Ammonia on Gallium Trifluoride Trihydrate. The hydrated fluoride was treated with liquid ammonia in a weighed, evacuated tube in a manner analogous to that employed in the preparation of the gallium bromide and gallium iodide ammonates. The system was evacuated to constant weight at room temperature. A white powder similar in appearance to the original salt resulted. The product was analyzed for ammonia and gallium according to the usual procedures which have already been described.

Anal. Subst., 0.3341, 0.0872; NH_3 , 0.0476, 0.0122. Calcd. for $\text{GaF}_3 \cdot 3/2 \text{H}_2\text{O} \cdot 3/2 \text{NH}_3$; NH_3 , 14.23. Found: 14.25, 14.02.

Anal. Subst., 0.0853, 0.0825; Ga_2O_3 , 0.0445, 0.0432. Calcd. for $\text{GaF}_3 \cdot 3/2 \text{H}_2\text{O} \cdot 3/2 \text{NH}_3$; Ga, 38.84. Found: 38.81, 38.95.

The analyses suggest strongly that half of the water of the trihydrate is replaced by ammonia molecules. This result is in accord with the fact that half of the water of the trihydrate is easily removed when the salt is subjected to a high vacuum at 140° , while the remaining water molecules are removed with great difficulty at this temperature under the same conditions. The results merely suggest the empirical formula given above as one possibility since the molecular weight of the complex is not known.

¹⁵ Observations by Mr. M. C. Crew.

¹⁶ Observations by Mr. M. C. Crew. The details of the dehydration of $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ will appear in a later paper on the preparation of anhydrous gallic fluoride.

The addition of ammonia to the anhydrous gallic fluoride might produce results of an entirely different nature. Studies are now being made in this direction.

Summary

Gallium tribromide and gallium triiodide react with liquid ammonia at -33.5° to form ammonates in which six molecules of ammonia are combined with the halide. The ammonates are stable at room temperature in the absence of moisture. It is shown that ammonia is readily displaced by water molecules when the ammonates are exposed to air. This process is found to be readily reversed in liquid ammonia.

The halides of gallium resemble those of indium and aluminium in their behavior with ammonia.

Two methods are given for the preparation of gallium trifluoride trihydrate.

The hydrated trifluoride is studied in liquid ammonia solution. A complex is formed in which one-half of the water is replaced by ammonia molecules.

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THE DIFFUSION OF GASES THROUGH FUSED QUARTZ

BY LIU SHENG T'SAI AND T. R. HOGNESS

In 1900 Villard¹ first observed that fused quartz, when heated to redness, was permeable to hydrogen. This observation was followed by a number of investigations²⁻¹³ on the diffusion of hydrogen, helium, neon, argon, oxygen, and nitrogen through fused silica and through various kinds of glass. Quantitative measurements of permeabilities for gases other than hydrogen and helium have not been made, and some of the qualitative observations are in disagreement.

Williams and Ferguson⁹ found that with gas pressures up to one atmosphere, and temperature to 881°C no leakage of air or nitrogen gas through silica glass was observed. Berthelot observed that both oxygen and nitrogen were present in an evacuated tube after heating in air for half an hour at 1300°C., while Wustner⁷ found that nitrogen diffused through quartz at 900°C and 1,000 atmospheres, and that under approximately the same conditions, oxygen did not. Mayer's⁸ observations showed that for pressures smaller than atmospheric neither oxygen nor nitrogen diffused through quartz, while for pressures greater than atmospheric this experimenter found an increase in diffusion with increase in pressure and temperature.

Williams and Ferguson and Van Voorhis also found that the silica glass is permeable to helium, and is easily observable at 180°C. The permeability is proportional to gas pressure, and, according to the former of these observers, is an exponential function of the temperature.

Richardson and Richardson⁴ observed that neon diffused through quartz at about 1000°C. After one hour's heating in air a faint blue argon spectrum and a yellow helium line were obtained, while prolonged heating resulted in the more fully developed spectra of both helium and neon. The argon spectrum, they concluded, was due to the trace of air absorbed by the wall of the tube before heating.

In preparation for later experiments it was found desirable to have better data on the permeability of quartz glass for some of these gases, so we have undertaken quantitative determinations of this property.

Apparatus and Experimental Procedure

The diffusion cell consisted of a thin tube of clear fused quartz, the thickness of which was measured by three different methods: (1) measurement with calipers, (2) calculation of the thickness from the weight of water displaced by the quartz tube, the density and the area of the immersed portion of the quartz tube being known, (3) by the same method as (2) except that mercury was used instead of water. The average of these measurements gave a thickness of 0.033 cm. After the thickness had been determined the tube

was sealed off at one end and at the other end it was sealed to a quartz capillary which was in turn connected to the McLeod gauge through a quartz-pyrex graded seal. Around the cell, which had the dimensions of 1.46 cm outside diameter by 16 cm, a heavy-wall quartz test tube was fitted to hold the gas. To ensure the air-tightness of the necessary glass-rubber connection, which was of such length that it was far away from the furnace, DeKhotinsky cement was used. In addition, an electric fan was used to facilitate the cooling.

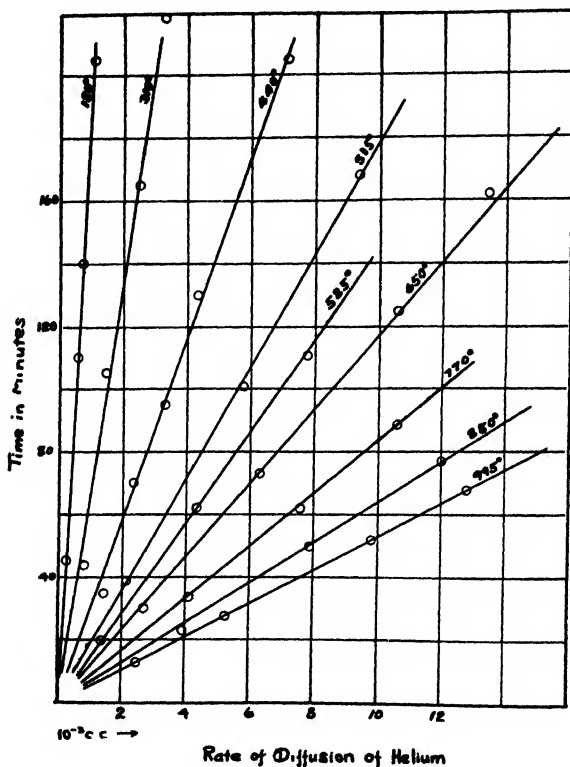


FIG. 1

After the apparatus was set up the whole system was evacuated for about three days. At the end of this time the pressure in the apparatus was less than 1×10^{-5} mm but on standing for about twelve hours the pressure increased to about 2×10^{-4} mm. The casing was then evacuated and the gas in question was introduced. The system was evacuated during the time that it took for the furnace to reach temperature equilibrium, about three hours, after which time the pump was disconnected and the measurements were begun. The increase in pressure was determined with a McLeod gauge at regular intervals of time, and such results as were obtained for neon and helium are shown in Figs. 1 and 2. As has been noted, there was a slight increase of pressure with time due to the desorption of the gas from the glass

walls. It was, therefore, necessary to make this correction for the gases which diffuse rather slowly. This was done by noting the rate of increase of pressure of the system while the cell was at the temperature under investigation and the casing evacuated. The difference between the apparent rate obtained in the usual manner, and this blank rate gave the actual rate due to diffusion. When these corrections were taken into consideration no definite diffusions were observed for nitrogen, oxygen, and argon. In the case of argon, spectroscopic tests showed that diffusion of this gas took place at the highest temperatures, but that the rate was not enough to offer any quantitative data.

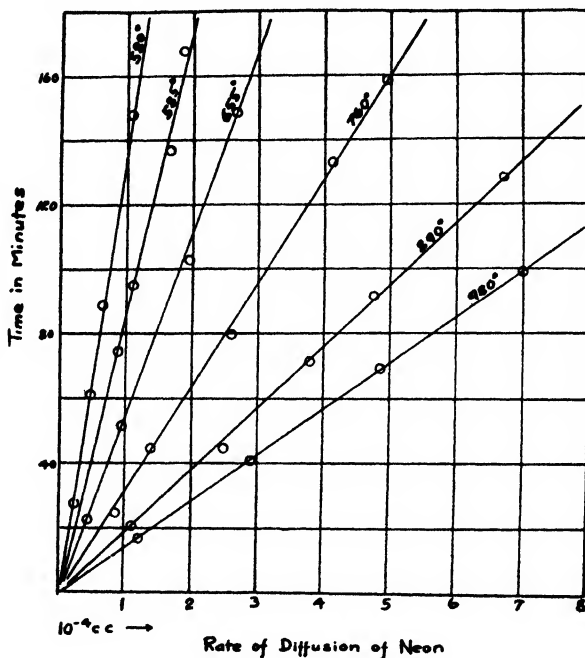


FIG. 2

Preparation of Materials

Helium was supplied in a pure form by the United States Bureau of Mines, and was used without further purification.

Neon, supplied by the Air Reduction Company, was purified three times by fractional condensation with activated charcoal at liquid air temperature. Any helium present in the original neon was removed in this way.

Argon, supplied by the same company, was used without purification.

Oxygen was prepared by heating potassium chlorate and manganese dioxide. The gas was led through a phosphorus pentoxide tube before using.

Nitrogen was prepared by heating a solution of sodium nitrite and ammonium chloride. The gas was purified by passing it through a tube containing dry potassium hydroxide and then over phosphorus pentoxide.

Discussion of Results

Permeability is here defined as the rate in cubic centimeters (measured at 0°C and 760 mm) per hour at which the gas at one atmosphere pressure diffuses into vacuum through a wall 1 mm thick and 1 square centimeter in area. Table I shows the permeability of quartz glass for both helium and neon at different temperatures. The calculation of these values was made by assuming that the rate of diffusion is inversely proportional to the thickness of the wall, an assumption which, according to the mathematical formulation

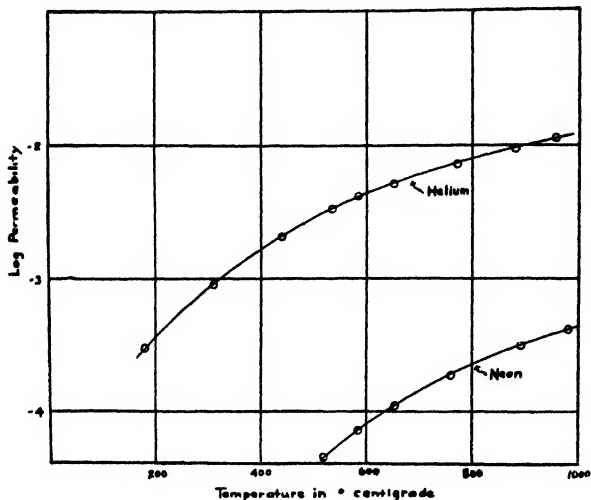


FIG 3

of the simple theory of diffusion, is a valid one for thin walls.⁷ The plot of the logarithms of the permeability against temperature for these two gases is shown in Fig. 3.

In as much as the permeability of glass increases very rapidly with the temperature, it has been assumed that this function is an exponential one. Williams and Ferguson, from measurements at three temperatures, concluded that in the case of helium such an exponential relationship existed. More observations, however, were necessary to indicate the real trend of the curve. Our results show that the increase in permeability with temperature is somewhat less than that which the exponential relationship demands. For the permeability of helium at 440° and at atmospheric pressure, Williams and Ferguson obtained a value of 39×10^{-4} cc, Van Voorhis, approximately 25×10^{-4} cc, while we get a value of 21×10^{-4} cc. As shown by these authors, different samples of silica glass gave different values of the permeability for hydrogen, so we do not expect a better check than this. The permeabilities for helium and neon at 900°C and atmospheric pressure are 100×10^{-4} and 3.2×10^{-4} , or in the ratio 31 to 1, respectively. Williams and Ferguson found a ratio of 22 to 1 for helium and hydrogen at 500°C and 760 mm.

TABLE I
Permeability for Helium

Temperature	Permeability $\times 10^4$	Log Permeability
180°C	3	-3.523
310	9	-3.046
440	21	-2.678
535	33	-2.482
585	42	-2.377
650	51	-2.293
770	72	-2.143
880	94	-2.027
955	113	-1.947

Permeability for Neon

520°C	.45	-4.347
585	.70	-4.155
655	1.10	-3.959
760	1.85	-3.733
890	3.15	-3.502
980	4.20	-3.377

If the increasing permeability with increasing temperature were due solely to the increased velocity of the permeating molecules one would expect the permeability to increase as the square root of the temperature. This is very far from the case. The quartz glass must be regarded as possessing channels¹⁴ which increase in clearance with increasing temperature. As shown by X-ray analysis,¹⁵ silica glass, when heated for thirty minutes at 700°C, undergoes marked devitrification. This undoubtedly increases the channels for the diffusing gas, increasing the permeability. We found that silica glass, when heated to high temperatures, undergoes a permanent change which results in a noticeably greater permeability for helium. Since different samples of quartz glass give slightly different results, and since the permeability depends somewhat upon the previous heat treatment of the glass, the absolute values we give here are for one particular sample only, and cannot be applied too exactly in other calculations.

As one would expect, the permeability of quartz glass for various gases is greater for the atoms or molecules of smaller cross section. Our positive result for argon is undoubtedly real but the value of the permeability of quartz for this gas was so low that its measurement was impossible. The heavier rare gases would undoubtedly diffuse so slowly as to prohibit detection, if any diffusion at all took place.

References

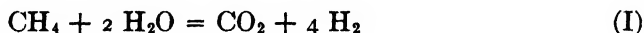
- ¹ Villard: Compt. rend., **130**, 1752 (1900).
- ² Jaquerot and Perrot: Compt. rend., **139**, 789 (1905).
- ³ Berthelot: Compt. rend., **140**, 821 (1905).
- ⁴ Richardson and Richardson: Phil. Mag., **22**, 704 (1911).
- ⁵ Bodenstein and Kranendieck: Nernst Festschrift, 100 (1912).
- ⁶ Mayer: Phys. Rev., **6**, 283 (1915).
- ⁷ Wustner: Ann. Physik, **46**, 1095 (1915).
- ⁸ Cardoso: Science Abstracts, **25A**, 732.
- ⁹ Williams and Ferguson: J. Am. Chem. Soc., **44**, 2160 (1922).
- ¹⁰ Piutti and Lera: Men. Accad. Lincei, (v) **14**, 125 (1923).
- ¹¹ Elsey: J. Am. Chem. Soc., **48**, 1600 (1926).
- ¹² Van Voorhis: Phys. Rev., (A) **23**, 557 (1925).
- ¹³ Baxter, Starkweather, and Ellestad: Science, **68**, 516 (1928).
- ¹⁴ Zachariason: Work to be published in the J. Am. Chem. Soc.
- ¹⁵ Randall, Rooksby, and Cooper: Krist., **75**, 707 (1930).

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METHANE EQUILIBRIA FROM ABSOLUTE ENTROPIES, WITH A NOTE ON THE USE OF THE EHRENFEST SYMMETRY NUMBER

BY A. R. GORDON AND COLIN BARNES

The entropy of methane at 298°K was calculated from spectroscopic data by Giauque, Blue and Overstreet¹ who used the Ehrenfest formula which is strictly valid for the rotational entropy at this temperature. A calculation by Villars,² using the rotational symmetry characters of Elert,³ gave the same result when corrected for some numerical errors.⁴ The value so obtained for the entropy agreed moderately well with the free energy data derived by Storch⁵ from the measurements made by Randall and his associates on the two reactions



The calculations of Storch, however, involved specific heats which are not in agreement with those calculated from the vibration spectrum of methane. A consistent computation, using spectroscopic entropies and heat capacities of the gases, may now be carried out for these reactions; the only other quantities that are involved are the "third law" entropy of graphite and the calorimetric values of the heats of reaction.

1. The Entropy of Methane from 300° to 1200°K

In the calculations mentioned above, only a single temperature was considered; for the present purpose it is necessary to compute the entropy of methane up to 1200° in order to cover the equilibrium data on reactions I and II.

The molar translational entropy for temperature T and pressure 1 atmosphere for a gas of molecular weight M ($= 16.036$) is given by the usual Sackur-Tetrode formula⁶

$$S_T = -2.295 + 3R/2 \ln M + 5R/2 \ln T \quad (1)$$

The values of this expression for the various temperatures are entered in Table I.

¹ Giauque, Blue and Overstreet: *Phys. Rev.*, (2) **38**, 196 (1931).

² Villars: *Phys. Rev.*, (2) **38**, 1552 (1931).

³ Elert: *Z. Physik*, **51**, 6 (1928).

⁴ MacDougall: *Phys. Rev.*, (2) **38**, 2074 (1931).

⁵ Storch: *J. Am. Chem. Soc.*, **53**, 1266 (1931).

⁶ The values of the constants used are (*Handbuch der Physik*, 1926): $R = 1.9858 \text{ cal./deg.}$; $k = 1.372 \times 10^{-16} \text{ ergs/deg.}$; $h = 6.55 \times 10^{-27} \text{ erg. sec.}$; $N = 6.06 \times 10^{23}$; 1 atm. = $1.0133 \times 10^6 \text{ dynes/cm}^2$.

The methane molecule, considered as a completely symmetrical rigid rotator, has three equal moments of inertia $A = B = C = 5.17 \times 10^{-40}$, given by the measurements of Dickinson, Dillon and Rasetti¹ on the Raman effect in methane; if I be written for \sqrt{ABC} , such a model gives a classical rotational entropy

$$S_R' = 3R/2 + 3R/2 \ln 8\pi^7/3 kT/h^2 \quad (2)$$

when *all* the rotational levels are taken into account. From the work of Elert,² however, it is known that only one-twelfth of the rotational states in methane are to be retained, for this is the fraction of all the molecular states which belong to a definite symmetry class, either completely symmetrical or completely antisymmetrical. For temperatures ranging from 300° to 1200°, the state sum (see note on symmetry number below) for the rotational entropy is just 1/12 of the value used in the derivation of S_R' ; i.e. if S_R' is to be retained, we must subtract $R \ln 12$ from it to get the value of the rotational entropy of methane. This is, of course, what is meant by saying that the CH₄ molecule has a "symmetry number" 12.

The weight g of the lowest electronic configuration is 1 and will not enter into the complete expression for the entropy. The four hydrogen atoms in the methane molecule (for the temperature range considered) contribute, due to their intrinsic spins, an entropy $4R \ln 2$; thus the quantity S_R , entered for various temperatures in Table I, is given by

$$S_R = S_R' - R \ln 12 + 4R \ln 2 \quad (3)$$

The fundamental vibration frequencies have been given by Dennison;³ they are

$$4217 \quad (1) \qquad 1520 \quad (2) \qquad 3014 \quad (3) \qquad 1304 \quad (3)$$

in cm⁻¹, where the number in brackets after a frequency indicates its degree of degeneracy, i.e. the number of times it must be supposed to occur in calculating the state sum for the vibrational entropy S_V . S_V , computed in the usual way, is entered in Table I for the various temperatures. The total entropy is given by

$$S = S_T + S_R' + S_V - R \ln 12 + 4R \ln 2 = S_T + S_R + S_V \quad (4)$$

and is entered in Table I. The table also contains values of the heat capacity of methane at constant pressure for the temperatures considered; the vibrational contributions were computed from the fundamental frequencies of the molecule in the usual manner.

¹ Dickinson, Dillon and Rasetti: Phys. Rev., (2) 34, 582 (1929).

² Elert; Loc. cit.

³ Dennison: Astrophys. J., 62, 84 (1925); Dennison and Ingram: Phys. Rev., (2) 36, 1451 (1930).

TABLE I

Molar Entropy and Heat Capacity at Constant Pressure (1 atmos) of Methane

T°K.	S _T	S _R	S _V	S	C _P
300	34.288	15.612	0.108	50.01	8.54
400	35.716	16.469	0.429	52.61	9.71
500	36.824	17.134	0.971	54.93	11.09
600	37.729	17.677	1.666	57.07	12.46
700	38.494	18.136	2.458	59.09	13.71
800	39.157	18.534	3.301	60.99	14.87
900	39.742	18.884	4.181	62.81	15.90
1000	40.265	19.198	5.066	64.53	16.83
1100	40.738	19.482	5.954	66.17	17.67
1200	41.170	19.741	6.833	67.74	18.45

2. The Equilibrium I

If P_X is the partial pressure of a component X in this reaction and if K be defined by

$$K = P_{CH_4} \cdot (P_{H_2O})^2 / P_{CO_2} \cdot (P_{H_2})^4$$

then

$$R \ln K = -Q/T + \Sigma S \quad (5)$$

where Q is the heat of reaction at temperature T and

$$\Sigma S = S_{CH_4} + 2S_{H_2O(g)} - S_{CO_2} - 4S_{H_2}$$

the entropies being all for temperature T and pressure 1 atmosphere.

The heat of combustion of methane¹ at 298° is 212790 cal., and the heat of formation of water¹ at the same temperature is 68313 cal.; from these two numbers and the heat of vaporization² of water at this temperature (10485 cal.), $Q_{298} = -39500$ cal. The values of Q for higher temperatures can now be found by integration of the specific heat curves, the heat capacities for methane being given in Table I and the values for the other gases having been previously calculated.³ The values of Q/T so obtained are given in Table II. Values of ΣS , obtained from the methane entropies in Table I and the known entropies of the other gases³ are entered in Table II, which also gives the resulting values of $R \ln K$. From the latter the curve in Fig. I was constructed.

TABLE II

The Equilibrium $CH_4 + 2 H_2O = CO_2 + 4 H_2$

T°K.	575	600	625	650	675	700
-Q/T	74.08	71.40	68.92	66.62	64.48	62.49
- ΣS	49.03	49.49	49.87	50.24	50.59	50.90
R ln K	25.05	21.91	19.05	16.38	13.89	11.59

¹ Rossini: Bur. Standards J. Research, (6) 1, 36 (1931).

² Int. Crit. Tables, 5, 138.

³ Gordon and Barnes: J. Phys. Chem., 36, 1143 (1932).

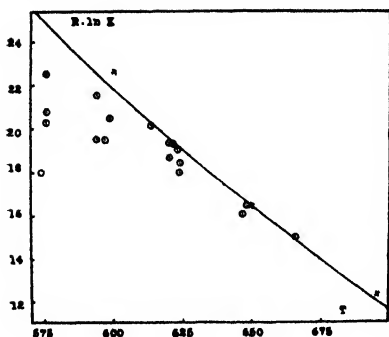


FIG. 1

The experimental numbers obtained by Randall and Gerard¹ for this reaction are shown in the same figure; the small circles indicate values obtained in approaching equilibrium from the CO_2 — H_2 side, and the crosses those obtained in approaching equilibrium from the CH_4 — H_2O side. As is evident from the figure, the agreement between the calculated and observed values of $R \ln K$ is quite satisfactory; the use of spectroscopic entropies and specific heats has removed the discrepancy supposed to exist between the calculated and observed entropy change for the reaction. The values² suggested for this reaction are $-\Delta H^\circ_{298.1} = -39500$, $-\Delta S^\circ_{298.1} = -41.52$, $-\Delta F^\circ_{298.1} = -27120$.

3. The Equilibrium II

In this reaction the entropy of graphite gives rise to the most uncertainty, as there is always an element of risk when using a calorimetric entropy in conjunction with spectroscopic entropies. Fortunately an independent check is available here, since the equilibrium constant for the reaction



is fairly accurately known.³ Using the equation of Magnus⁴ for the heat capacity of graphite, and the value 1.22 calories per degree for the entropy of graphite⁵ at 273.1° , the entropy for the three temperatures 1123° , 1173° and 1223° is found to be 6.47, 6.70 and 6.92, respectively. The entropies of carbon monoxide and carbon dioxide can be found by interpolation from Gordon and Barnes' Tables IV and V,⁶ giving -41.58 , -41.47 and -41.35 as the values of $(S_{(\text{Graph})} + S_{\text{CO}_2} - 2S_{\text{CO}})$ for the three temperatures. From the heat of combustion of graphite,⁷ viz. 94420 cal. at 291° , and that of carbon monoxide⁸ (67623 cal. at 298°), $Q_{298} = -40826$, so that Q/T for 1123° , 1173° and 1223° is -35.63 , -34.00 and -32.50 , respectively; hence, $R \ln (P_{\text{CO}_2})/(P_{\text{CO}})^2$ for the three temperatures is -5.95 , -7.47 and -8.85 . The corresponding experimental numbers are -5.26 , -7.47 and -8.54 , in reasonably good agreement.

¹ Randall and Gerard: Ind. Eng. Chem., 20, 1335 (1928).

² The entropy of carbon dioxide at 300° is 51.09, not 51.19 as entered in Gordon and Barnes' Table V; the mistake arose from the value entered for S_V at this temperature; this should be 0.738, not 0.838 as printed.

³ Rhead and Wheeler: J. Chem. Soc., 97, 2178 (1910).

⁴ Int. Crit. Tables, 5, 94.

⁵ Int. Crit. Tables, 5, 87.

⁶ Gordon and Barnes: Loc. cit.

⁷ Roth and Wallasch: Z. Elektrochemie, 21, 1 (1915); Roth: 26, 288 (1920).

⁸ Rossini: Loc. cit.

From the heats of combustion of methane and graphite, and the heat of formation of water, the heat of formation of methane at 298° is 18256 cal.; from this and the heat capacities of graphite, methane (Table I) and hydrogen,¹ the values of Q/T entered in Table III are found by tabular integration. The entropies of methane (Table I), of hydrogen¹ and of graphite² lead to the values of $\Sigma S = S_{(\text{Graph.})} + 2S_{\text{H}_2} - S_{\text{CH}_4}$ entered in that table. The resulting values of $R \ln (P_{\text{H}_2})^2/(P_{\text{CH}_4})$ are shown by the curve in Fig. II.

TABLE III

The Equilibrium $\text{C}_{(\text{Graph.})} + 2\text{H}_2 = \text{CH}_4$

T°K	700	800	900	1000	1100	1200
Q/T	29.68	26.51	23.96	21.87	20.10	18.58
ΣS	24.88	25.47	25.90	26.21	26.45	26.63
$R \ln K$	-4.80	-1.04	+1.94	+4.34	+6.35	+8.05

The same figure shows the relation of the calculated curve to the experimental values obtained by Mayer and Altmayer,³ by Randall and Mohammed⁴ and by Coward and Wilson;⁵ the forward reaction, i.e. methane synthesis, gives the points indicated by the light symbols; the reverse reaction gives those indicated by the black symbols. For the lower part of the temperature range the calculated curve lies satisfactorily with regard to the experimental points, but the agreement is not so close at higher temperatures where the experimental curve would lie about 1 cal./degree below that of the figure.

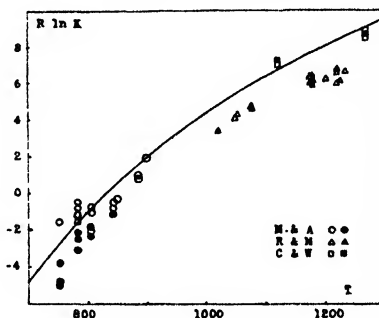


FIG. 2

Villars⁶ has recently suggested frequencies for the methane molecule somewhat different from those used above, but in better agreement with observed Raman lines; he replaces Dennison's single frequency 4217 cm^{-1} by the Raman frequency 2914.8 but leaves the other frequencies unchanged. This makes an appreciable difference in the entropy and heat capacity of methane⁷ only for

¹ Gordon and Barnes: Loc. cit.

² The graphite entropies were computed from the entropy at 273.1° by tabular integration of $(C_p/T) \cdot dT$; they are

T°K	700	800	900	1000	1100	1200
S	4.15	4.76	5.33	5.86	6.36	6.83

³ Mayer and Altmayer: Ber., 40, 2134.

⁴ Randall and Mohammed: Ind. Eng. Chem., 21, 1048 (1929).

⁵ Coward and Wilson: J. Chem. Soc., 115, 1380 (1919).

⁶ Villars: Preprint of papers to be presented at the New Orleans meeting of the American Chemical Society, March 30, 1932, Paper No. 32.

⁷ Using Villars' frequencies, the numbers are (cf. Table I):

T°K	700	800	900	1000	1100	1200
S	59.12	61.05	62.90	64.66	66.33	67.94
C_p	13.86	15.11	16.22	17.21	18.09	18.90

temperatures greater than 700° . As far as the calculation of $R \ln K$ for Reaction II is concerned, however, the changes introduced in Q/T and ΣS partly cancel, and thus the equilibrium constant is only slightly altered; the use of Villars' frequencies would change -1.04 for 800° into -1.05 and $+8.05$ for 1200° into $+8.00$, far too small a correction to account for the discrepancies shown in Fig. II.

The satisfactory agreement in the case of Reaction I would indicate that the quantities used in the calculations are not very seriously in error. A reasonable explanation for the drift in $R \ln K$ for Reaction II at the higher temperatures lies in the experimental conditions under which equilibrium was attained; side reactions leading to the formation of hydrocarbons other than methane undoubtedly occur,¹ particularly at high temperatures, and low values of K would result from the measured excess of methane. In view of the experimental difficulties on the one hand, and the uncertainties inherent in the calculation of a vibration-rotation entropy on the other, the agreement in this case also is probably as close as can be expected.

The value of $-\Delta F^\circ_{298.1}$ for methane,² calculated from the heat of formation and the entropies, is 12490 cal.

4. Note on the use of the "Symmetry Number"

From the work of Gibson and Heitler³ and of Ludloff,⁴ it is now known that the Ehrenfest symmetry number, σ , originally introduced as a geometrical concept into the classical phase space of a gas, is merely a convenient way of expressing what fraction of all the energy states of a molecule have a certain symmetry character; the expression "symmetry character" is to be understood in the sense of quantum mechanics as applied to molecules containing two or more identical nuclei. If the energy states ϵ_n of a molecule occur with the weight factors p_n , the familiar entropy expression is

$$S = R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \quad (6)$$

where Σ_1 (the state sum) and Σ_2 (the energy sum) are defined by

$$\Sigma_1 = \sum p_n \cdot e^{-\epsilon_n/kT}; \quad \Sigma_2 = \sum p_n \cdot (\epsilon_n/kT) \cdot e^{-\epsilon_n/kT} \quad (7)$$

For temperatures above 300°K , the evaluation of these sums, for practically all types of molecules, leads to the classical expression for the rotational entropy, provided no states are rejected on a basis of selection of some definite type of symmetry. In the computation of such an entropy, however, we must select only those states of a certain symmetry; the correction to the classical expression is then summarized in a symmetry number. It appears that when no enumeration of the rotational symmetry characters can be made, no symmetry number can be deduced with certainty from an assumed geometrical

¹ See Storch: *Loc. cit.*; Pring and Fairlie: *J. Chem. Soc.*, 101, 91 (1912).

² Giauque, Blue and Overstreet's value (*loc. cit.*) is 12440.

³ Gibson and Heitler: *Z. Physik*, 49, 465 (1928).

⁴ Ludloff: *Z. Physik*, 57, 227 (1929).

model; even in simple cases the geometrical concept can only be made to give the desired number by some device or other, which essentially involves a knowledge of the rotational characters themselves.

In the case of models of some exact geometrical figure, e.g. a regular tetrahedron, it is often possible from the wave equation of the molecule, to find the fraction of the rotational levels which are, say, symmetrical in the nuclei; this fraction is one-twelfth in methane, one-third in ammonia, and so on. But if the molecule only roughly approximated to a regular figure, it would then possess no symmetry number suggested by geometry. A small continuous deformation of the regular figure will change its moments of inertia continuously, and it is known that the rotational energy values are continuous functions of the moments of inertia, so that the energy values will themselves change continuously; for example, if the deformation of a symmetrical methane molecule (three equal moments of inertia $A = B = C$) be such that A , B and C are no longer equal, the $(2J + 1)^1$ originally coincident rotational levels for a given J will proceed to separate under the deformation into $(2J + 1)$ distinct levels each $(2J + 1)$ -fold degenerate. Now the symmetry character of a level (and therefore its weight) is invariant for a deformation of the molecule; thus Hund² used the deformation of a symmetrical top to establish the symmetry characters for an unsymmetrical rotator; hence the entropy given by Eq. 6 must be a continuous function of the moments of inertia, and must only change slightly as a result of a small deformation. All geometric symmetry has by now been lost, however, and no symmetry number in the Ehrenfest sense can be assigned. Of course, when one keeps in mind the quantum significance of σ , this difficulty vanishes; the fraction of states of given symmetry character will be conserved for small deformations from geometric symmetry, and it would still be necessary in Eq. 3 to use $\sigma = 12$ for a methane molecule which need only roughly approximate to a regular tetrahedron.

¹ GIAUQUE, Blue and Overstreet: Loc. cit.

² Hund: Z. Physik, 43, 822 (1927). To be precise, permissible deformations must result from perturbations symmetrical in the like particles.

The necessity for the invariance of the symmetry characters during a deformation is evident when one considers the question of nuclear spin. With four hydrogen nuclei in the molecule, Villars (loc. cit.) has shown that there are five $S(4)$ spin wave functions, three $S(3+1)$ each threefold degenerate, and one doubly degenerate $S(2+2)$ —sixteen in all. From the work of Elert (loc. cit.) one twelfth of the rotational states in methane are $S(4)$, nine twelfths are $S(3+1)$ and two twelfths are $S(2+2)$. If Σ is the value of the State Sum in the absence of symmetry and spin (see Eq. 2), then its high temperature value (to a close approximation) in the presence of symmetry and spin will be

$$5 \times \Sigma/12 + 9 \times 1/9 \times \Sigma/12 + 2 \times (1/4 + 1/4) \times 2\Sigma/12 = 16\Sigma/12$$

(The factors $1/9$ and $(1/4 + 1/4)$ arise from the fact that only one ninth of the products of two $S(3+1)$ functions are $S(4)$, while one quarter of the products of two $S(2+2)$ are $S(4)$ and one quarter $A(4)$ both of which may be retained owing to the double character of the ground vibrational state). It is for this reason that the classical formula gives the rotational entropy of methane correctly if the classical expression is corrected by a symmetry term— $R \ln 12$ and a spin term $+R \ln 16$. That the spin contribution is just $R \ln 16$ is in conformity with the rule that at high temperatures spin entropy must cancel in the entropy of reaction.

Since the spin wave functions are independent of the geometrical arrangement of the particles, it is necessary that the rotational symmetries be unaltered during the deformation, since otherwise the spin contribution would no longer be $R \ln 16$.

In Cooley's measurements¹ on the infra red adsorption spectrum of methane, different fine structure separations are found for the bands 3.31μ and 7.7μ , corresponding to the existence of at least two different moments of inertia; this result is of course quite incompatible with a regular tetrahedral structure. Asymmetry is also indicated by the work of Langseth² on the Raman effect in carbon tetrachloride and carbon tetrabromide. If it should prove that only two of the methane moments of inertia are equal to 5.17×10^{-40} , while the third is, say, ten per cent larger, the rotational entropy given by Eq. 3 would be only 0.1 cal./degree greater than that entered in Table I, the symmetry number σ_2 being retained in accordance with the preceding argument. Conversely, if the use of a given symmetry number leads to an entropy in approximate agreement with experiment, this must not be used as evidence as to the exact "shape" of the molecule.

The use of the symmetry number, where geometrical symmetry is excluded, is illustrated by the following simple calculation:

(a) Consider an unsymmetrical pyramidal molecule RX_3 , whose moments of inertia are such that $(h^2/8\pi^2kT) \cdot (1/A, 1/B, 1/C) = 0.10, 0.09, 0.08$; the energy levels can then be found from the equations for an unsymmetrical rotator. Assume that the three X nuclei have no spin and are slightly different, e.g. three different isotopes. Then the weight factor for each of the $2J + 1$ rotational levels for a given J is simply $2J + 1$ since symmetry considerations are entirely excluded. The values of the energy and state sums are entered in the column *a* of the table below, together with the resulting value of the entropy obtained from Eq. 6; the expression S_R' (Eq. 2) is here applicable without correcting terms.

(b) If the three X nuclei are identical but non-spinning, then from a consideration of the limiting case as $A \rightarrow B < C$, for a given J the levels $\tau = J, J-5, J-6, J-11, J-12, \dots$ will be either symmetrical or antisymmetrical in the X nuclei, while for other values of τ the levels will have degenerate symmetry; thus since the lowest vibrational state is double, having both a completely symmetric and a completely antisymmetric character, the levels $\tau = J, J-5, J-6, \dots$ will have the weight $2J + 1$, the other levels having the weight zero. If Eq. 2 is to be used, a term $R \ln 3 (= 2.182)$ must be subtracted from the value of S_R' for case *a*, for the fraction one-sixth of the rotational levels can be associated with one of the lowest vibration symmetries, and a further fraction one-sixth with the second of the lowest vibration symmetries, so that one-third of the rotational-vibrational states are of a definite symmetry character.

(c) Finally, let each of the three X nuclei have one half unit of spin; the weights³ of the levels $\tau = J, J-5, J-6, \dots$ are then $4(2J + 1)$, the other levels receive the weights $2(2J + 1)$. If Eq. 2 is to be used, $-R \ln 3 + 3R \ln 2 (= 1.947)$ must be added to the expression on its right.

¹ Cooley: *Astrophys. J.*, **62**, 73 (1925).

² Langseth: *Z. Physik*, **72**, 350 (1931).

³ Villars: *Loc. cit.*, Table II.

	(a)	(b)	(c)
Σ_1	67.54	22.43	179.93
Σ_2	99.82	33.21	266.06
S_R (Eq. 6)	11.301	9.117	13.247
S_R (Eq. 2)	11.301	9.119	13.248
corrected.			

The table shews clearly that the rotational entropy, calculated by the classical Eq. 2, agrees with that obtained by evaluating the exact sums, when the classical expression receives the necessary corrections in the form of a symmetry number and a spin term. The table also shews that geometrical symmetry is a sufficient but not necessary condition for the existence of a symmetry number. It must be remembered, however, that the use of the classical formula for the rotational entropy, quite apart from corrections due to spin or to symmetry properties, is restricted to temperatures high enough for almost complete classical "excitation" of the rotational degrees of freedom. At lower temperatures the accurate summation formula must necessarily be used.

*The University of Toronto,
Toronto, Canada.
April, 1932.*

THE ROTATION OF ROCHELLE SALT IN ALKALINE MEDIA

BY ALAN NEWTON CAMPBELL AND ALEXANDRA JEAN ROBSON CAMPBELL

Introduction

In connection with work at present being carried out in this laboratory on the kinetics of racemisation, it was found necessary to determine the rotation of Rochelle salt in different strengths of NaOH. It was found that the specific rotation is very variable with alkali concentration and even changes sign at an alkali concentration of about 9 N.¹ Independent evidence was also furnished from determinations of OH' concentration in these solutions, of complex formation. That the variation of rotation in different media is a consequence of loose complex formation loading the molecule is no new hypothesis, although the experimental evidence in favour of this assumption is practically non-existent. It seemed to us that in the case of Rochelle salt in NaOH the variation was so large that definite experimental evidence in favour of complex formation might be obtained. We have therefore applied the following independent methods to the problem:

1. Determination of OH' concentration in sodium hydroxide solutions containing Rochelle salt.
2. Phase rule study of the system $\text{NaOH} - \text{NaKC}_4\text{H}_4\text{O}_6 - \text{H}_2\text{O}$.
3. Conductometric measurements.

The result has been to supply definite experimental evidence of complex formation.

Experimental

Mallinckrodt's U.S.P. Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$ and stick caustic soda were used in the preparation of all solutions. Solutions of sodium hydroxide were prepared by dissolving stick NaOH in water. Repeated analysis showed these solutions to contain only the merest trace of carbonate. Solutions, for all but the phase rule measurements, were always made by dissolving one-tenth of a mol of hydrated Rochelle salt in the appropriate NaOH, and making up to 100 c.cs. The use of hydrated Rochelle salt reduces the alkalinity of each solution by 7.5%, but the figures given everywhere refer to the original strength of the NaOH.

Specific Rotations of Molar Rochelle Salt in Sodium Hydroxide of Various Concentrations. The determinations of rotation were carried out in a Hilger 3-field instrument, using a 2 dm. tube. In the absence of a monochromator we were obliged to use a series of light filters, which, however, gave perfect matching of the fields. The filters were Wallace colour filters, having the following transmissions:

¹ Nature, 129, 281 (1932).

Filter No.	Transmission (\AA)	Arithmetic Mean
2	7608-6100	6854
3	7608-5800	6704
4	7608-5400	6504
5	7608-5300	6454
6	7608-5000	6304

Needless to say, the arithmetic means are not the optical means, so that the figures for specific rotation have not an absolute significance. The temperature of measurement was 22.2° throughout. The results obtained are shown in Table I.

TABLE I
Specific Rotations

Normality of NaOH	Filter Number				
	2	3	4	5	6
Pure Water	+25.2	+26.8	+28.1	+28.5	+28.5
1.10	+23.3	+25.2	+26.3	+26.8	+27.1
1.907	+21.7	+22.9	+24.0	+24.4	+24.5
2.72	+19.7	+20.8	+21.7	+22.1	+22.1
5.16	+13.1	+13.7	+14.4	+14.8	+14.9
6.97	+6.68	+6.99	+7.2	+7.4	+7.5
9.36	-0.43	-0.91	-1.12	-1.22	-1.26
14.18	-10.9	-12.0	-12.7	-12.7	-12.8

The negative rotations were quite stable in the cold, showing that no racemisation takes place in the cold.

Determination of OH' Concentration

Despite every precaution to purify the hydrogen, etc., the hydrogen electrode gave wavering and uncertain results in strongly alkaline solutions of Rochelle salt. Measurements based on the velocity of saponification of ethyl acetate were a little steadier but failed at high concentrations, owing to the increasing insolubility of ethyl acetate in strong alkali. It is well known that the quinhydrone electrode cannot be used in alkaline media. Perhaps the most satisfactory electrode turned out to be the manganese hydroxide electrode: this at least gave good comparative readings. All these measurements gave values for the OH' concentration lower in the solutions containing Rochelle salt than in the corresponding alkali alone, and indeed it was this which first led us to postulate complex formation. Nevertheless, we do not attach more than qualitative significance to the figures, which are given in Table II.

Conductometric Measurements. These were carried out by determining the molecular conductivity of the NaOH and molar Rochelle salt separately and then in mixed solutions. Simple additivity is not to be expected, but, according to the literature, the ionisation (or activity) of strong electrolytes

TABLE II

Concentration of NaOH	(OH) in NaOH alone	(OH) in NaOH R.S.	Method
1.10 N	0.775 N	0.117 N	Hydrogen Electrode
2.05 N	1.35 N	0.73 N	" "
2.03 N	—	0.41 N	" "
1.907 N	—	0.325 N	" "
1.07 N	—	0.103 N	" "
2.93 N	1.965 N	1.3 N	" "
1.1 N	—	0.147 N	Saponification of
1.9 N	—	0.81 N	Ethyl Acetate
2.95 N	—	0.78 N	" "
14.18 N	2.10 N	2.10 N	Manganese Hydroxide
9.36 N	2.817 N	1.75 N	Electrode

is not greatly affected by the presence of a second electrolyte with a common ion. However, a comparison experiment with mixed sodium and potassium chlorides was carried out. In similar work which is now being carried out with mandelic acid, and where it appears that complex formation, if it occurs at all, is only slight, the sodium hydroxide and mandelic acid reduce each other's conductivity only slightly.

No special precautions were taken, as this was not in itself a conductometric investigation, beyond placing the conductivity cell in a thermostat at 27.3°. The conductivity vessel was chosen to have a large cell constant (10.4) to prevent unduly high conductivities. The results are contained in Table III.

TABLE III

Substance and Concentration	μ obs.	Sum of μ of constituents	Diff.	Ratio
M/1 Rochelle Salt in Water	98	—	—	—
0.935 N NaOH	202	—	—	—
M/1 R.S. + 0.935 N NaOH	210	$202 + \frac{(98 \times 1000)}{935} = 306.5$	96.5	0.685
1.97 N NaOH	164	—	—	—
1.97 N NaOH + M/1 R.S.	124	214	90	0.58
2.72 N NaOH	158	—	—	—
2.72 N NaOH + M/1 R.S.	103	194	91	0.53
6.97 N NaOH	106	—	—	—
6.97 N NaOH + M/1 R.S.	52	120	68	0.435
13.9 N NaOH	36.2	—	—	—
13.9 N NaOH + M/1 R.S.	1.19	43.25	42.06	0.0275
N/1 KCl	121	—	—	—
N/1 NaCl	91	—	—	—
N/1 NaCl + N/1 KCl	188	212	24	0.89

Phase Rule Study

Determinations of the solubility of Rochelle salt in increasing concentrations of caustic soda were carried out in a thermostat at 25°. The wet solid phase was also analyzed and the results plotted by Schreinemaker's method. It is of course realised that, by the definition of a component, it must not undergo decomposition, whilst it is probable that in complex formation the Rochelle salt does decompose. Nevertheless, it was thought that the form of the curves would throw light on the matter, as indeed they do. The results are contained in Table IV.

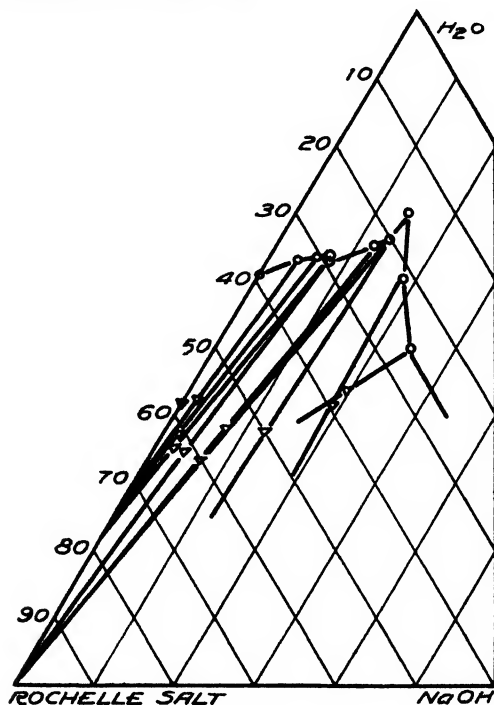


FIG. 1

Rochelle Salt, Caustic Soda and Water. Temp. 25°C.

TABLE IV

Exp. No.	Liquid Phase			Wet Solid Phase		
	R.S.	NaOH	H ₂ O	R.S.	NaOH	H ₂ O
1.	39%	—	61%	58%	—	42%
2.	33.3	3.7	63.0	56.0	1.68	42.33
3.	31.0	5.8	63.2	61.3	2.0	36.7
4.	29.0	7.25	63.75	62.5	2.6	34.9
5.	29.5	7.6	62.9	61.7	3.9	34.4
6.	20.2	13.5	66.3	60.3	6.1	33.6
7.	22.6	12.2	65.2	54.7	7.8	37.5
8.	16.1	13.85	70.05	50.0	12.5	37.5
9.	21.6	15.3	63.1	39.6	19.0	41.4
10.	25.7	23.9	50.4	36.9	19.4	43.7

Beyond the NaOH concentration of experiment 10 it was found impossible to proceed owing to the great viscosity of the solution. When the above figures are plotted on triangular paper, it becomes obvious that about 7% NaOH the solid phase becomes anhydrous Rochelle salt. About 13% NaOH a further point of inflection occurs. That the solid phase here is NaOH seems very improbable, judging by the direction of the tie-lines. In view of what was said at the beginning of this section, it is not to be expected that the tie-lines should intersect in this latter region. It is worthy of note that the points of inflection are accompanied by marked changes in the appearance of the solid phase. At the second point of inflection, the solid phase assumes a structure resembling a gel, whilst the liquid phase might be compared to a synerised liquid. As the concentration of NaOH is increased the bulk of the "gel" increases until eventually the liquid portion disappears or, at all events, becomes unfilterable by suction.

Conclusion

The specific rotations of Rochelle salt in various concentrations of alkali, and for different regions of the spectrum have been determined. The very marked variation is accounted for on the hypothesis of complex formation. This hypothesis receives considerable support from the experimental evidence presented. This rests upon:

1. Reduced OH' concentration in solutions of NaOH containing Rochelle salt.
2. Much reduced conductivity on mixing solutions of Rochelle salt and NaOH.
3. The form of the phase rule diagram.

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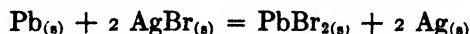
THERMODYNAMICS OF LEAD BROMIDE¹

BY JESSIE Y. CANN AND RUTH A. SUMNER

The purpose of this investigation is to determine, by means of electromotive force measurements, the free energy of formation, ΔF , the change of entropy, ΔS , the change in heat content, ΔH , and the activity coefficient, γ , of lead bromide.

Free Energy of Lead Bromide

The published measurements of the potential of the cell corresponding to the reaction



are not concordant. We therefore have measured the cell Pb (in Sat. Amalg.), $\text{PbBr}_{2(s)}$, $\text{PbBr}_{2(\text{sat.})} + \text{KBr}_{(\text{aq})}$, $\text{AgBr}_{(s)}$, $\text{Ag}_{(s)}$ in which the electrolyte was a saturated solution of lead bromide in 0.01, 0.025, and 0.1 M KBr to which a small amount of hydrobromic acid had been added.

The lead bromide used by J. Y. Cann was a portion of the same material which was used by Randall and Vietti,² and which had been re-crystallized four times from conductivity water.

The potassium bromide solution was prepared from high-grade "analyzed" material, and the hydrobromic acid was a dilute solution of a pure acid through which hydrogen had been bubbled to remove traces of bromine. The lead amalgam was of the same supply as that used for the determination of the potential of the lead electrode.³

The silver bromide spirals were prepared by electrolyzing silver oxide—silver spirals prepared as previously described,³ in a 0.1M solution of potassium bromide. The lead amalgam and spirals were freed from absorbed film or gases, and the solutions introduced as described previously.³

The cells were the ordinary H-cells of Pyrex, and the thermostat was either the ordinary oil thermostat regulated for 25°, or the one used by Gerke, fitted with an easily adjustable thermo-regulator. The thermometer was a mercury thermometer which was checked against a standard resistance thermometer that had been calibrated by the U. S. Bureau of Standards.

Nine cells were made up. Cells 1, 2, 3, and 4 contained 0.01 M KBr. The first cell, which had lead bromide only over the lead amalgam, gave un-

¹ This problem was suggested by Merle Randall, and the experimental part of the work was started at the University of California by J. Y. Cann on sabbatical leave from Smith College, and continued by R. A. Sumner at Smith College as partial fulfillment of the requirements for Special Honors in Chemistry. Charlotte Klingler, Graduate Student at Smith College, has repeated the results of the authors, having made four cells, each of which gave a steady constant value of $E_{298.1}^\circ = 0.3465$, agreeing precisely with the results obtained previously.

² Randall and Vietti: J. Am. Chem. Soc., 50, 1526 (1928).

³ Randall and Cann: J. Am. Chem. Soc., 52, 589 (1930).

satisfactory results and was discarded. No. 2, a large cell, gave $E_{298.1} = 0.3531$ V which gradually decreased to 0.3519 V. This contained only 0.5 cm. layer of solid lead bromide in each side of the H-cell. No. 3, a very small cell, with a larger quantity of solid lead bromide, gave 0.3482 V at 25° after about seven days; but after standing in the thermostat for over thirty days the potential became constant at $E_{298.1} = 0.3469$ V which agrees with the potential of three other cells. No. 4, the same type of cell as No. 2, gave a very constant potential of 0.3498 V during about two weeks; but we feel, in view of later developments, that the amount of solid lead bromide (1 cm layer) was not sufficient. Cell No. 5 contained 0.1 M potassium bromide and enough solid lead bromide to completely cover the silver-silver bromide spiral. The cell was taken through the temperature range from 15° to 42° and back again four times, and about seventy-five values, taken after the initial erratic period of three days, during which time the value of the potential rapidly decreased at the constant, initial temperature of 25° , were plotted, a few of which (taken at random) are shown in Table I. Cell No. 6 contained 0.025 M potassium bromide, was erratic and discarded. Cells No. 7 and 8 contained 0.025 M potassium bromide with enough solid lead bromide to fill the cell to the middle of the cross of the H. No. 7 was taken through the temperature cycle twice and agreed with Cell No. 5. Cell No. 8 was high at the beginning, but after the traverse of a temperature cycle of fourteen days, agreed with the previous cells. Cell No. 9 contained 0.1 M potassium bromide with a very large amount of solid lead bromide and gave results in agreement with Cells 3, 5, 7 and 8. Random potentials of these cells are given in Table I.

Nine cells were prepared by R. A. Sumner.

Numbers 1 and 2 contained 0.1 M KBr,
 3 and 4 contained 0.01 M KBr,
 5 and 6 contained 0.05 M KBr, and
 7 and 8 contained 0.025 M KBr.

These cells were made up in exactly the same manner as the last and best ones prepared by J. Y. Cann. Numbers 5 and 7 gave erratic values and were discarded. Numerous readings, over a period of a year, were taken on cells 1, 2, 3, 4, 6 and 8, and Table II gives a list of representative values at various temperatures.

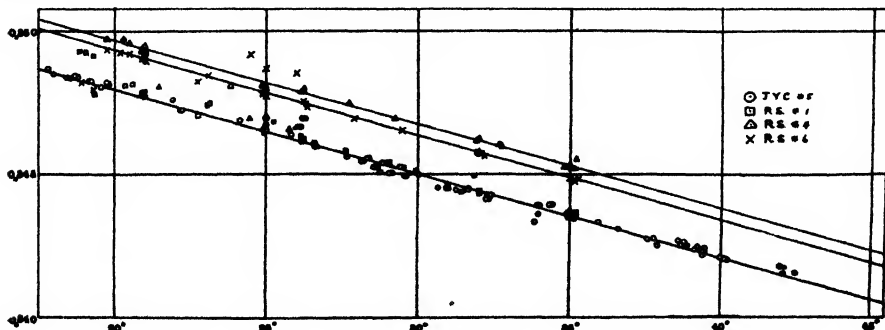


FIG. 1

In addition, four cells were prepared by C. Klingler. These all contained 0.1 M KBr. These last cells came to equilibrium within a day or two and gave steady, constant values of $E^\circ_{298.1} = 0.3465$ at 25°C . This checking of results by three independent workers convinces us that our method of preparing the cells and the values obtained, are correct.

Curve I shows the measured potentials of the best cells.

All the measured potentials were plotted against the temperature and from the best average curve we find

$$E_{298.1} = 0.3465\text{V}; dE/dt(298.1) = -0.000289 \text{ V/o.}$$

Whence

$$\begin{aligned} \text{Pb (in sat. amalg.)} + 2 \text{AgBr}_{(s)} &= \text{PbBr}_{2(s)} + 2 \text{Ag}_{(s)}; \\ \Delta F_{298.1} &= -15995 \text{ cal.}, \Delta S_{298.1} = -13.34 \text{ Cal./o}; \\ \Delta H_{298.1} &= -19972 \text{ cal.} \end{aligned} \quad (1)$$

Combining with the data of Gerke⁴ for the formation of saturated lead amalgam, we find

$$\begin{aligned} \text{Pb}_{(s)} + 2 \text{AgBr}_{(s)} &= \text{PbBr}_{2(s)} + 2 \text{Ag}_{(s)}; \Delta F^\circ_{298.1} = -16258 \text{ cal}; \\ \Delta S^\circ_{298.1} &= -12.599 \text{ cal./o}; \Delta H^\circ_{298.1} = -20014 \text{ cal.} \end{aligned} \quad (2)$$

Then combining with Randall and Halford's⁵ value for

$$2 \text{Ag}^\circ + \text{Br}_2^\circ = 2 \text{AgBr}; \Delta F^\circ_{298.1} = 2 (-22917) \text{ we find} \quad (3)$$

$$\text{Pb}^\circ + \text{Br}_2^\circ = \text{PbBr}_2; \Delta F^\circ_{298.1} = -62092 \text{ cal.} \quad (4)$$

This value is in good agreement with the value of Latimer⁶ i.e. $\Delta F^\circ_{298.1} = -62,065$ Cal. It also agrees with that of Krahmer⁷ i.e. $\Delta F^\circ_{298.1} = -62057$ cal.

Combining our value $\Delta S_{298.1} = -12.599$ for

$\text{Pb}_{(s)} + 2 \text{AgBr}_{(s)} = \text{PbBr}_{2(s)} + 2 \text{Ag}_{(s)}$ with $\Delta S^\circ_{298.1} = -0.96$ for AgBr obtained from the reaction $\text{S}_{\text{Ag}^\circ} + \text{S}_{\text{Br}^\circ} \rightarrow \text{S}_{\text{AgBr}^\circ}$, using the values $\text{S}_{\text{Ag}^\circ} = 10.25$, $\text{S}_{\text{Br}^\circ} = 16.3$ and $\text{S}_{\text{AgBr}^\circ} = 25.59$ ⁸ we find for the reaction, Elements

$$\text{PbBr}_2; \text{S}^\circ_{298.1} = -14.519, \quad (5)$$

whereas Latimer⁶ obtains -12.63 ; thus showing a difference of 1.889 entropy units. It was because of this difference, dependent upon the temperature coefficient of the cell, dE/dT , that the experimental work has been checked by three individuals.

Combining $\Delta H^\circ_{298.1} = -20014$ for the reaction $\text{Pb} + 2 \text{AgBr} = \text{PbBr}_2 + 2 \text{Ag}$ with Bichowsky's⁹ value of $\Delta H^\circ_{298.1} = -23840$ for AgBr, we obtain $\Delta H^\circ_{298.1} = -67694$ for $\text{Pb} + \text{Br}_2 = \text{PbBr}_2$ (6)

⁴ Gerke: J. Am. Chem. Soc., **44**, 1684 (1922).

⁵ Randall and Halford: J. Am. Chem. Soc., **52**, 192 (1930).

⁶ Latimer and Hoenshel: J. Am. Chem. Soc., **48**, 19 (1926).

⁷ Krahmer: Z. Elektrochemie, **26**, 97 (1920).

⁸ The value 25.59 is an average of 25.62, obtained by Eastman and Milner (personal communication) and 25.56 obtained by Eucken, Clusius and Woitinek: Z. anorg. Chem., **203**, 39 (1931).

⁹ Intern. Crit. Tables, Vol. V.

For this value Gerke¹⁰ obtained -67480 .

Using the third law and our values of $\Delta F^\circ_{298.1} = -62092$ and of $\Delta S^\circ_{298.1} = -14.519$, we find $\Delta H^\circ_{298.1} = -66420$. Braune and Koref¹¹ found $\Delta H^\circ_{298.1} = -66350$. If now we use Latimer's⁸ value of $\Delta S^\circ_{298.1} = -12.63$ for PbBr_2 , and employ the third law, we find $\Delta H^\circ_{298.1} = -65857$. Krahmer⁷ found $\Delta H^\circ_{298.1} = -65580$ and Thomsen¹² found -64456 . We take the value of $\Delta H^\circ_{298.1} = -67694$ as correct.

Activity Coefficient of Lead Bromide

Randall and Vietti² have determined the solubility of PbBr_2 in KBr solutions. They state that by graphical methods they have been unable to determine the activity coefficient of PbBr_2 in KBr consistent with other data. Using their data and plotting $\log 1/m \pm$ against $\mu \frac{1}{2}$, and extrapolating to zero concentration, we found the proportionality factor 46.82. Then by dividing any value of $1/m \pm$ by this value,¹³ we found the corresponding value of the activity coefficient, $\gamma \pm$. Table III gives a tabulation of these values.

TABLE III

M KBr	M PbBr ₂	m \pm	log 1/m \pm	1/m \pm	$\mu \frac{1}{2}$	$\gamma \pm$
0.001	0.02645	0.0425	1.3715	23.5215	0.2835	0.5024
0.002	0.02611	0.0425	1.3716	23.5302	0.2834	0.5025
0.005	0.02500	0.0423	1.3738	23.6471	0.2828	0.5050
0.01	0.02345	0.0423	1.3732	23.6162	0.2835	0.5044
0.02	0.02043	0.0423	1.3737	23.6423	0.2851	0.5049
0.025*	0.01845*	0.0413	1.3835	24.1847	0.2835	0.5165
0.05	0.01380	0.0436	1.3601	22.9157	0.3023	0.4894
0.1	0.00859	0.0490	1.3094	20.3008	0.3546	0.4355
0.2	0.00694	0.0682	1.1661	14.6589	0.4684	0.3131
0.374	0.00687	0.1011	0.9953	9.9893	0.6282	0.2113

* Interpolated value.

In order to determine the activity coefficient from *electromotive force* measurements, use is made of the following equation: $E = -3RT/2F \ln (k^1 \gamma \pm m \pm)$, in which¹⁴ the constant k^1 , which includes E° , may be found by substituting a value of $\gamma \pm$, found by some other method, together with the appropriate values for the related quantities, and solving for k^1 . For this purpose we chose Randall and Vietti's value of $\gamma \pm$ in 0.01 m KBr soln, and found the value of k^1 to be 0.0058411. Using this value, $\gamma \pm$ for the other concentrations of KBr was calculated. The values thus obtained for the concentrations 0.025, 0.05 and 0.1 m are as follows:

¹⁰ Gerke: Chem. Reviews, 1, No. 4, 377 (1925).

¹¹ Braune and Koref: Z. anorg. Chem., 87, 175 (1914).

¹² Thomsen: Landolt-Börnstein Tabellen, 2, 1533 (1923); J. prakt. Chem., (2), 12, 92 (1875).

¹³ Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," 371 (1923); J. Am. Chem. Soc., 43, 1112 (1921).

¹⁴ Ref. 12, p. 355.

m KBr	$\gamma \pm$ E.M.F.	$\gamma \pm$ Sol'y.
0.025	0.51661	0.5165
0.05	0.48936	0.4894
0.1	0.43543	0.4355

The solubility data are listed for purposes of comparison. It will be seen that these values of $\gamma \pm$ from electromotive force measurements are practically identical with those obtained from solubility measurements. Too much weight, possibly, should not be laid upon this identity because the method of calculation was relative, not absolute. Nevertheless the agreement is remarkable.

We also calculated the product, $K_{s.p.} = 4m \pm^3 \gamma \pm^3$, for $PbBr_2$, and found it to be 0.0000389.

Recent papers by Fromherz¹⁵ discuss the activity coefficients of the lead halides in great detail. He states repeatedly that the true activity coefficients of an electrolyte like $PbBr_2$ agree closely with those of the strong electrolyte $BaCl_2$. Our results are in general accordance with this statement.

Summary

We have calculated the values of ΔF , ΔH and ΔS for the formation of lead bromide from its elements. Our values of ΔF and ΔH agree reasonably well with those found in the literature. Our value of ΔS differs from Latimer's value because the coefficient dE/dT would seem to be too large.

We have also calculated the values of the activity coefficient from both electromotive force measurements, using our own data, and from solubility measurements, using the data of Randall and Vietti. A relative method of calculation was used.

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¹⁵ Fromherz: *Z. physik. Chem.*, **153**, 376; 321 (1931).

THE POLYIODIDES OF RUBIDIUM

I. Iodine and Rubidium Iodide

BY T. R. BRIGGS AND E. S. PATTERSON

Temperature-composition data for the system iodine and potassium iodide and for the system iodine and cesium iodide, at a pressure of approximately one atmosphere, have been reported in earlier papers¹ in this series. In the first of these systems, no solid compound (such as KI_3) was found in equilibrium with the melt, whilst in the second system the compounds (polyiodides) CsI_3 and CsI_4 were definitely shown to be produced.² The present communication presents the data for the system iodine and rubidium iodide, which system, as it will appear in the sequel, turns out to be intermediate as regards the other two.

The experimental technique employed in this investigation was the same as that described in the earlier papers and needs no further comment. The data required for the construction of the phase diagram were obtained from temperature arrests in the cooling curves, from the boiling points of mixtures of known composition and from analyses of saturated liquid phases (melts). The method used in the analysis will be found in the earlier papers.

The iodine was purified by being sublimed and it was dried carefully before it was used. The rubidium iodide (from Kahlbaum) was recrystallized once from water and then dried. The combined iodine in the product was then determined by analysis and it was found to be 97.8 per cent of that required by the formula RbI . The salt was thus considered to be sufficiently pure for the purpose of the investigation.

The various types of data which were obtained are presented in Tables I, II and III.

The temperature-composition diagram is shown in Fig. 1. The solid triiodide RbI_3 certainly exists below 188° , but there is no indication of a higher polyiodide such as RbI_4 , analogous with CsI_4 . The triiodide melts incongruently at about 188° , decomposing into RbI and iodine above this temperature. The solubility of RbI in iodine, like that of KI and of CsI , is almost independent of the temperature; and because of this, no temperature arrest due to the separation of solid RbI was discernible in the cooling curve for Mixture 12 in Table I. The (constant) boiling point of melts saturated with RbI lies at about 238° and a special determination of the eutectic point made it possible to place the latter at 80.8° and 17.4 mole per cent RbI .

¹ Briggs and Geigle: *J. Phys. Chem.*, **34**, 2250 (1930); Briggs: **34**, 2260 (1930).

² Cf. also the ternary system iodine, cesium iodide and water. Briggs, Greenawald and Leonard: *J. Phys. Chem.*, **34**, 1951 (1930).

TABLE I
Temperature Arrests (°C)

Mixture Number	Mole Per Cent RbI	1st Arrest	2nd Arrest
1	0	114	none
2	5	108.8	80.6
3	10	100.0	80.8
4	15	87.0	80.8
5	17	81.8	80.8
6	20	103	80.7
7	25	134	81.0
8	30	149	81.0
9	35	167	80.0
10	40	178	81.0
11	42.5	185	81.5
12	45	187.2	79.0
13	47.5	187.8	79.0
14	50	188	none
15	52.5	187.5	none
16	55	187.5	none
17	60	189	none
18	65	188	none
19	70	190	none
20	85	189	none

TABLE II
Composition of the Saturated Liquid

A. Original Mixture containing 42 Mole Per Cent RbI		B. Original Mixture containing 55 Mole Per Cent RbI	
Temperature	Mole Per Cent RbI	Temperature	Mole Per Cent RbI
81 (eutectic)	17.44	195	44.71
142	26.35	206	45.23
160	32.16	220	45.62
175	37.60	238.5 (B. P.)	46.23

TABLE III
Boiling Points (°C)

Mixture Number	Mole Per Cent RbI	Boiling Point	Mixture Number	Mole Per Cent RbI	Boiling Point
1b	0	184	6b	50	*236
2b	10	187	7b	60	*238.5
3b	20	195	8b	70	*238.5
4b	30	207	9b	80	*238
5b	40	225	10b	90	*239

* Constant, others rising with time.

Wells, Wheeler and Penfield,¹ in their celebrated investigation of the polyiodides, reported the existence of RbI_3 as solid phase in aqueous systems of iodine and rubidium iodide. They were unable to prepare a higher polyiodide of rubidium, such as RbI_5 , analogous with the higher polyiodide of cesium, to which they had assigned the formula CsI_5 .² They stated that the triiodide

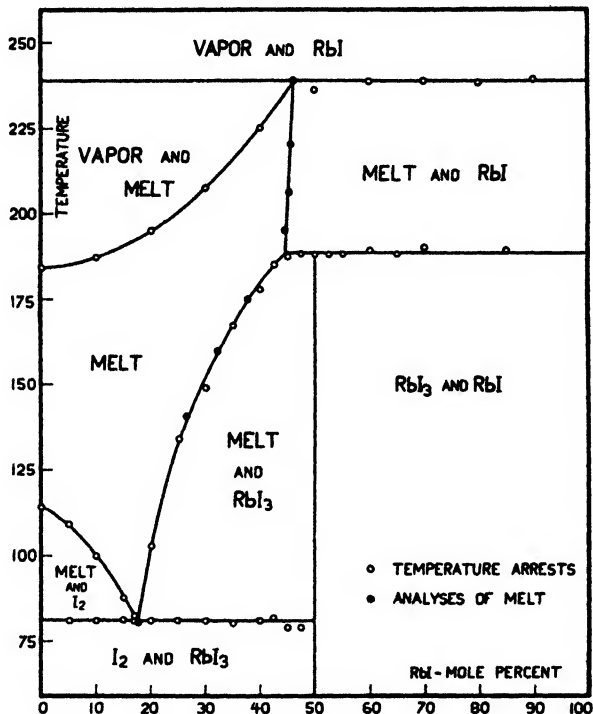


FIG. 1
The System I_2 — RbI at approximately 1 atm.

“melts” at 194° in an open tube and at 190° in a closed tube, and that it “whitens” at 270° because of the loss of the polyhalide iodine. The “melting” point of Wells and his coworkers is evidently the transition point (188°) for the system RbI_3 , RbI and melt. Their temperature of whitening, however, is unnecessarily high, for the melt saturated with RbI boils at 238° and the vapor must consist virtually of pure iodine. The present investigation thus confirms in all essential respects, the findings of Wells, Wheeler and Penfield. It also confirms the work of Foote and Chalker,³ who showed that a single polyiodide, presumably RbI_3 , exists as solid phase in the ternary system iodine, rubidium iodide and water at 25° .

Abegg and Hamburger,⁴ in their work on the ternary system containing benzene, reported the higher polyiodides RbI_7 and RbI_9 in addition to the

¹ Am. J. Sci., (3), **43**, 475; **44**, 43 (1892).

² Cf. Briggs, Greenawald and Leonard: J. Phys. Chem., **34**, 1951 (1930); Briggs: **34**, 2260 (1930).

³ Am. Chem. J., **39**, 561 (1908).

⁴ Z. anorg. Chem., **50**, 403 (1906).

triiodide RbI_3 . There is no indication of these higher polyiodides in the binary system, and if they do exist in the ternary system, it seems reasonable to suppose that they must be ternary compounds containing benzene.¹

In that part of their paper which deals with the binary system iodine and potassium iodide, Abegg and Hamburger stated that a mixture of iodine and rubidium iodide, corresponding in composition to the supposed compound RbI_3 , melted at 81.3° . It is now apparent that this is the eutectic temperature and not the melting point of a compound; Abegg and Hamburger were not dealing with RbI_3 , as they supposed, but with a mixture of iodine and RbI_3 . They made the same mistake here that they made in the system iodine and potassium iodide—that is to say, they took the eutectic temperature to be the melting point of a polyiodide. The probable explanation of this curious error and the consequences which it produced have been discussed at length in the paper by Briggs and Geigle.

In connection with the work reported in this paper, various other systems containing a halogen and an alkali-metal halide have been investigated. These systems were: iodine and sodium iodide, iodine and sodium chloride, iodine and sodium bromide, iodine and potassium chloride, iodine and potassium bromide, bromine and potassium bromide. The temperature arrests and the boiling points of mixtures of known composition showed that in every case the components are immiscible. The same is true of calcium iodide and iodine as a binary system, but it is interesting to find that investigation of the ternary system iodine, calcium iodide and water, now under way in this laboratory, shows that iodine is extremely soluble in mixtures of calcium iodide and water, and that at least one *hydrated* calcium polyiodide is present as solid phase in the ternary system at 25° . We thus find no polyiodide of calcium in the binary system and not even any dissolving of calcium iodide by liquid iodine, yet the miscibility is extraordinarily great in the ternary system containing water and there is evidence of a polyiodide when water is the third component. This is strong confirmation of the position taken by Grace and accepted by Foote and Bradley.

Summary

The results of this investigation may be summarized as follows:

1. The temperature-composition diagram for the system iodine and rubidium iodide has been determined from 60° up to the boiling point of the saturated melt (238°).
2. The solid phases in contact with melt are iodine, rubidium triiodide (RbI_3) and rubidium iodide. The triiodide melts incongruently at 188° . No indication of a higher polyiodide, analogous for example with cesium tetraiodide, was obtained.
3. Iodine and rubidium iodide, as one would expect, is thus intermediate between iodine and potassium iodide (solid phases iodine and KI) and iodine and cesium iodide (solid phases iodine, CsI_4 , CsI_3 and CsI).

*Cornell University,
June, 1932.*

¹ Cf. Grace: J. Chem. Soc., 1931, 594; Foote and Bradley: J. Phys. Chem., **36**, 683 (1932).

OSMOTIC PRESSURE AND THE PERMEABILITY OF MEMBRANES

BY W. W. LEPESCHKIN *

Introduction

The author's experiments twenty years ago showed that the variation movements of plants are caused by a change of the turgor pressure in the pulvinus cells produced by the variation of the permeability of protoplasm to substances dissolved in the cell sap. Turgor pressure is a hydrostatic pressure caused by osmotic pressure. Thus the problem of the influence of the permeability of protoplasm upon turgor pressure is really a problem of the influence of the permeability of a membrane upon the hydrostatic pressure in the osmometer. This problem interested not only physiologists but also chemists, since no other explanation than the permeability of the membrane could be given for the discrepancy between the osmotic pressure calculated according to the van't Hoff-Arrhenius formula and that observed in an osmometer. If it was not this explanation, one had to admit with Kahlenberg¹ that osmotic pressure and gas laws are different, and although the new porous disc method of measuring osmotic pressure seems to be able to annihilate all doubt concerning the similarity of these laws, the problem of the cause of a too low pressure in the osmometer can scarcely be considered as solved.²

One explains a too low pressure in the osmometer mostly by the supposition that due to the penetration of the solute through the membrane the solvent under the membrane is gradually transformed into a more and more concentrated solution, the osmotic pressure of which brings that of the solution in the osmometer into a partial equilibrium. This supposition lies in the basis of Tammann's considerations of the dependence of the pressure observed in an osmometer upon the permeability of membranes to solutes.³ Tammann came to the conclusion that the ratio $P - P_b / 2P$ where P is the theoretical osmotic pressure calculated according to Arrhenius and van't Hoff and P_b is the pressure observed in the osmometer, is approximately constant and proportional to the permeability of the membrane to the solute.

A quite different principle lies in the basis of v. Antropoff's calculation of the dependence of the pressure in an osmometer upon the permeability of the membrane.⁴ Supposing that the solution formed under the membrane is continuously replaced by the solvent, v. Antropoff came to the conclusion that the pressure in an osmometer should depend not only upon the permeability of the membrane to the solute but also upon that to the solvent. Indeed,

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¹ Kahlenberg: *Trans. Wisconsin Acad. Sci.*, **15**, 209 (1906).

² R. V. Townend: *J. Am. Chem. Soc.*, **50**, 2958 (1928); F. T. Martin and L. H. Schultz: *J. Phys. Chem.*, **35**, 638 (1931).

³ G. Tammann: *Z. physik. Chem.*, **9**, 97 (1892).

⁴ A. von Antropoff: *Z. physik. Chem.*, **76**, 721 (1911).

the pressure in an osmometer is actually produced by the penetration of the solvent through the membrane into the osmometer and results in consequence of an increase of the volume of the liquid in the osmometer. But this volume depends not only upon the volume of the solvent coming into the osmometer but also upon the volume of the solute going out of the osmometer through the membrane. The maximum pressure in the osmometer is evidently reached when both volumes become equal. V. Antropoff gives the following formula which expresses the dependence of the maximum pressure in the osmometer P_m upon the permeability of the membrane to solvent σ' and that to solute σ : $P_m = P(1 - \sigma/\sigma')$ where P is the theoretical osmotic pressure. The testing of this formula was made by v. Antropoff on the basis of Cohen and Commelin's experimental data concerning the osmotic pressure of sugar-pyridin solutions. Comparing the calculated and experimental values of the pressure in the osmometer given in v. Antropoff's paper we may come, however, to the conclusion that the former are always greater than the latter, and sometimes the calculated pressure is more than twice as great as the observed one. V. Antropoff promised to give later his own experimental data concerning the same problem, but these data were not published during the next twenty years. The present experiments have as a purpose the explanation of the discrepancies just mentioned and show that Tammann's results as well as those of v. Antropoff should be considered in finding a mathematic scheme of the dependence of the hydrostatic pressure in the osmometer upon the permeability of the membrane.

Osmometer and Determination of the Maximum Hydrostatic Pressure

The maximum hydrostatic pressure in the osmometer was determined in the present experiments by the method similar to that used by Berkeley and Hartley,⁵ that is by finding a pressure in the osmometer which just prevents the sucking of water into the osmometer. The membrane used was parchment paper obtained from the Thomas Co., Philadelphia. Preliminary experiments showed that this membrane could be used for several months without any visible change of its chemical properties, being not affected by water or bacteria. This parchment paper had an average thickness of 0.180 mm. and soaked with water was thicker by twenty percent. The membrane was attached to an osmometer (o, Fig. 1) made of glass and fastened to a brass ring r to which the membrane m was stuck with a mixture of black sealing wax and venetian turpentine. The edges of the membrane were covered with a brass ring R attached to it by means of the same mixture. Both rings were pressed together by six brass clamps c which were gradually screwed on while the rings were heated and sealing wax melted. In order to fill all small cavities inside of parchment paper with water the osmometer was immersed in boiled and cooled water for some days (water surface covered with oil). The osmometer filled with a solution was then closed with a rubber stopper through which a thermometer t (divisions 0.1°C) and a glass tube a were inserted, and placed in water of a thermostat bath (Freas', capacity 50 liters). Water was

⁵ Earl of Berkeley and E. G. J. Hartley: *Phil. Trans.*, **206A**, 481 (1906); **209**, 177 (1909).

continuously stirred in the latter. The temperature in the osmometer was always adjusted to $25^{\circ}\text{C} \pm 0.02^{\circ}\text{C}$. Water used for the bath as well for the solutions in the osmometer was spring water (laboratory tap water). It contained 0.029 percent dissolved substances (CaO 0.004%, MgO 0.002%, K_2O and Na_2O 0.003%, Cl 0.092%, SO_3 0.004%, SiO_2 0.003%, CO_2 0.008%) and had $\text{pH} = 7.3$.

The tube a (Fig. 1) was connected (thick wall rubber tube) with the other part of the instrument in which the volume of water filtered through the membrane or sucked into the osmometer was measured. This part consisted

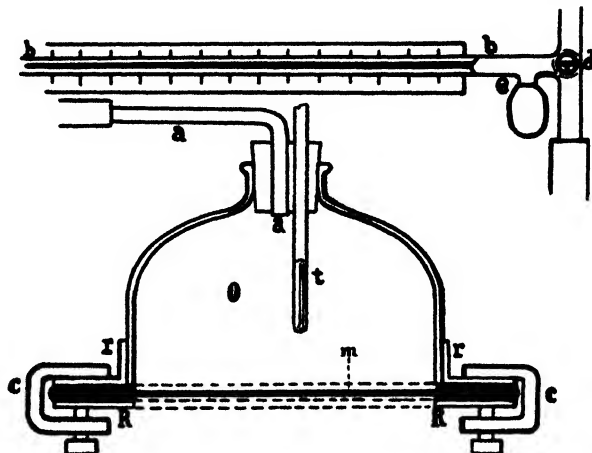


FIG. 1

Osmometer. Explanation is given in the text. The black line on the scale is thicker at the right than at the left.

of an exactly horizontal capillary tube b provided with a three channel glass cock d, the upper branch of which was connected with a funnel and served for filling the instrument with water or with the same solution with which the osmometer was filled. Air bubbles were carefully driven out. The lower branch of the cock was united with the osmometer by a thick wall rubber tube. The capillary tube had a short branch e provided with a rubber ball which could be squeezed by means of a clamp and served for filling the capillary tube with the liquid when it was disconnected from the funnel but connected with the osmometer. In this case the filtration of water through the membrane produced a movement of the meniscus in the capillary tube to the right, the sucking in of water its movement to the left. Every movement of the meniscus in the capillary tube by one division of the millimeter scale corresponded to 0.002015 cc of water passing through the membrane. The height of the capillary tube above the water level in the thermostat bath represented the pressure expressed in cm of the column of water or the solution used. In tables below the pressure is expressed in cm of water column. When the pressure used was greater than 200 cm it was produced by mercury. For this purpose a U-shape tube was inserted between the osmometer and the capillary tube, and the latter as well as a half of the U-shape tube was filled with mercury.

The same osmometer was used for the filtration of water and solutions to determine the permeability of the membrane to water, and for the determination of the osmosis rate of the solute through the membrane (permeability to solute). The diameter of the lower opening of the osmometer covered by the membrane, and therefore that of the part of the membrane through which the filtration or osmosis took place was 7.4 cm. The area of this part after the osmometer was filled with water or solutions and the membrane stretched was about 55.6 sq. cm. The volume of the osmometer was 289 cc. Every change of temperature in the osmometer by 0.1°C produced therefore a movement of the meniscus in the capillary tube by 3.7 divisions. This was considered in all experiments. In a few experiments (indicated below) the osmometer was immersed in a cement trough of a sink (cubic form, capacity 45 liters), filled with water. In this case the temperature varied more, and the correction was necessary.

Preliminary experiments showed that by the stretching of the membrane an increase of the pressure in the osmometer was completed in two to three hours when this increase was greater than 100 cm of water column. A smaller change of the pressure correspondingly required less time for the settlement of the equilibrium. About two hours were necessary for the temperature equilibrium. Accordingly, the observation of the meniscus always began three hours after the immersion of the osmometer in the thermostat bath and its connection with the capillary tube. The pressure was changed several times until a pressure was found which did not produce any filtration or sucking in of water through the membrane during a certain period of time (one to four hours). This pressure was considered as equal to the maximum pressure which can be reached in the osmometer. The concentration of the solution in the latter was determined immediately after the determination of this pressure.

Sodium chloride (Merck, blue label) was used in these experiments as solute. Its concentration was determined by titration with silver nitrate (potassium chromate as indicator). From the amount of chlorine found in the solution its amount contained in water was subtracted.

Is the Accumulation of Solute under the Osmometer responsible for a too Low Pressure?

It is well known that the maximum hydrostatic pressure in the osmometer with parchment paper as a membrane is many times smaller than the osmotic pressure calculated according to the van't Hoff-Arrhenius formula. Is the accumulation of solute in water under the osmometer responsible for this low pressure? Even if the solute passing through the membrane should form a solution under the membrane which falls down at the bottom of the vessel, one could think that a layer of the solution always remains under the lower surface of the membrane balancing by its osmotic pressure the most part of the osmotic pressure in the osmometer. It is very easy to prove, however, that a continuous stirring of the liquid under the osmometer does not increase the hydrostatic pressure in the osmometer. The following experiments prove

that even the removal of the very thin layer of the solution from the lower surface of the membrane does not increase the maximum hydrostatic pressure in the osmometer noticeably.

Experiment 1.—The osmometer was filled with a solution of sodium chloride, 0.1425 g-mol in a liter, and immersed in a sink trough filled with water. No stirrer was used this time. The temperature in the osmometer varied from 26°C to 26.6°C. The maximum hydrostatic pressure was found to be 122 cm of water column. The final concentration of sodium chloride in the osmometer was found to be 0.1298 g-mol. The theoretical osmotic pressure of this solution (calculated according to the formula $P = iRCT$) is 5795 cm of water column.

Experiment 2.—The above experiment was repeated but modified. The osmometer was filled with the solution of sodium chloride of the same concentration, and the maximum hydrostatic pressure found was 110 cm. Then a strong current of water from a glass tube (diameter 1.5 cm) was directed on the membrane of the osmometer from below. This current gave 12 liters of water in one minute. The distance between the tube opening and the membrane was 4 cm. When directed toward water surface the current gave a water jet of about one meter above the surface. The temperature in the osmometer varied from 25.5 to 26.1°C. In about 50 minutes the maximum hydrostatic pressure in the osmometer increased to 116 cm. This increase might result from a decrease of the stretching of the membrane. After the water current was stopped the maximum hydrostatic pressure decreased again, and it was found to be 109 cm. The final concentration of sodium chloride was found to be 0.1250 g-mol. The corresponding theoretical osmotic pressure is 5580 cm.

Experiment 3.—The concentration of the solution of sodium chloride in the osmometer was 0.0669 g-mol in a liter. The maximum hydrostatic pressure found was 53 cm. After a water current of 180 liters an hour was conducted into the trough at a distance of 20 cm from the osmometer the maximum hydrostatic pressure in the latter increased to 54 cm. Then the water current was directed on the membrane from below. In one hour the pressure was found to be 59 cm. The final concentration of the solution in the osmometer was 0.0645 g-mol. The theoretic osmotic pressure corresponding to this concentration is 3173 cm of water column. Temperature variations in the osmometer did not surpass 0.4°C.

From the experiments cited we may conclude that the removal of solute from the lower surface of the membrane does not affect noticeably the maximum hydrostatic pressure in the osmometer. Thus, the accumulation of the solute under the membrane is not responsible for the low pressure in the osmometer. It is evident that the penetration of the solute through the membrane affects this pressure in some other way. We may try now to elucidate this way.

Theoretical Aspect of the Problem

It should be emphasized that the problem of the dependence of the maximum hydrostatic pressure in the osmometer upon the permeability of the

membrane should be distinguished from that of the dependence of osmotic pressure upon this permeability. We may consider first the latter problem. This problem seems at first incomprehensible because one defines osmotic pressure as a thermodynamic value independent of any membrane. If we define it, however, as a force necessary to separate solvent from solute, as Nernst does⁶ and if we try to separate the former from the latter by means of a membrane, we will find that this force is greater in the case of a complete impermeability of the membrane to solute than in the case of its permeability. Indeed, a membrane which is permeable to solute can not separate the solvent from the solute completely. Also from the standpoint of the kinetic theory of osmotic pressure is the influence of the permeability of a membrane to solute on osmotic pressure comprehensible. Indeed, the osmotic pressure which can be considered from this standpoint as a sum of strikes on the membrane produced by molecules of solute is evidently greater if all molecules moving toward the membrane strike it than is the case when some of these molecules do not strike the membrane but penetrate through it, and this independent of whether the penetrating substance accumulates on the other side of the membrane or not.

Should we define osmotic pressure as a force which causes the solvent to penetrate into the solution through the membrane or as a force preventing this penetration, we will find that this force is smaller in the case of a permeable than of an impermeable membrane because this force results from the difference in concentration of the solute on two boundaries of the membrane and this difference is smaller when the solute penetrates the membrane. Even if we continuously replace the solution accumulating under the membrane by pure solvent, the force causing the solvent to pass into the solution through the membrane will be smaller because the layer of the solution adjacent to the membrane would always have a smaller concentration than that of the whole solution. Another question is whether such an incomplete force could be called osmotic pressure.

We may propose to call osmotic pressure, as it is usually done, a force necessary for a complete separation of the solvent from the solute, or resulting from a molecular bombardment of full strength, or necessary to prevent the passing of the solvent through the membrane when the latter is completely impermeable to the solute. We will call, however, the reduced force resulting from a certain permeability of the membrane to the solute *suction force of the solution*. We may try now to find the dependence of this force upon the permeability of the membrane to the solute. Let us suppose we have a cylindrical vessel closed at both ends in which a piston made of a semipermeable membrane separates a solvent from a solution of a substance in the same solvent. We now move the piston in the direction of the solution so that the volume of the latter is diminished by a very small value Δv while the solvent passes from the solution through the piston on its other side. We produce a work equal to $P \Delta v$ where P is the osmotic pressure of the solution. If the

⁶ Nernst, W.: "Theoretical Chemistry," English transl. by L. Codd, 136 (1923).

piston is permeable not only to the solvent but also to the solute, this work is smaller than $P \Delta v$ because not the whole solute contained in the volume Δv is separated from the solvent. If the solute penetrates during the movement of the piston in such an amount through the latter that it would form a solution in the volume Δv of the solvent which has an osmotic pressure p , the work we produce by the movement of the piston is equal to $P \Delta v - p \Delta v$. As the rate of diffusion of the solute through the piston can be supposed to be proportional to the osmotic pressure P and to the permeability of the membrane to the solute, the osmotic pressure p is proportional to both. If μ is a number proportional to the permeability of the membrane to the solute, we can conclude that the work done is equal to $P \Delta v - \mu P \Delta v$ or $P(1 - \mu)\Delta v$. The force with which this work is done is equal to $P(1 - \mu)$, and this force is evidently the suction force of the solution at the membrane of which the piston is made. The work done by the movement of the piston is evidently independent of the permeability of the latter to water, because we can move the piston with a desirable speed, and the work done remains the same. We may write therefore $P_o = P(1 - \mu)$ where P_o is the suction force of the solution, P is the osmotic pressure of the solution and μ is a number proportional to the permeability of the membrane to the solute.

A similar formula expressing the dependence of the suction force of the solution can be deduced from Tammann's formula mentioned in the introduction. Indeed, if M is a number proportional to the permeability, we may write: $(P - P_b)/2P = M$ or $P_b = P(1 - 2M)$. This formula expresses, however, the hydrostatic pressure in the osmometer only in the case when the permeability of the membrane to solvent is so great that the penetration of the solute through the membrane producing a change of the volume of the liquid in the osmometer can be disregarded. In order to get an exact idea about the maximum hydrostatic pressure in the osmometer one should consider with v. Antropoff that this pressure results from the entering of the solvent into the osmometer and that the increase of the volume of the liquid in the latter is diminished by the exosmosis of the solute. It is evident, however, that v. Antropoff's "treibende Kraft der Osmose" is really the suction force of the solution. Thus P in his formula is equal to $P(1 - \mu)$ where P is the osmotic pressure of the solution, and the formula expressing the dependence of the maximum hydrostatic pressure P_m in the osmometer should be written as follows:

$$P_m = P(1 - \mu)(1 - \mu/\sigma)$$

In this formula μ is a number proportional to the permeability of the membrane to the solute, σ is proportional to that to the solvent, and P is the osmotic pressure of the solution in the osmometer. We may call μ and σ permeability factors for solute and solvent. It should be emphasized that this formula concerns the case when the solvent under the membrane into which the solute diffuses from the osmometer, is continuously renewed. If the membrane is both sides in touch with a solution, the formula should be written as follows: $P_m = [P_a(1 - \mu/\sigma) - P_b](1 - \mu)$ where P_a is the osmotic

pressure of the solution inside, and P_b is that of the solution outside the osmometer. We are now going to test this formula on parchment paper. But in its application to the experiments described below one can simplify it. Namely, the volume of water into which the osmosis of the solute took place was in these experiments about 170 times greater than that of the solution in the osmometer, and the concentration of the solute in the outer liquid was at the end of the experiment in most cases more than 500 times smaller than that in the osmometer. Thus, without committing an error which surpasses the error unavoidable in the determination of the maximum hydrostatic pressure in the osmometer, we may omit P_b in the formula and test the formula: $P_m = P(1 - \mu)(1 - \mu/\sigma)$.

Dependence of the Maximum Hydrostatic Pressure upon Osmotic Pressure

From the above formula it follows that the ratio P_m/P should be constant if the permeability of parchment paper to water and sodium chloride is independent of the concentration of the latter. We may try whether this ratio is really constant.

The osmometer filled with a solution of sodium chloride (the concentration is given in Table I) was suspended above the water surface of the thermostat bath in a water vapor saturated atmosphere for three hours while the pressure in the osmometer was raised to a height corresponding to the maximum hydrostatic pressure found in a preliminary experiment. One could avoid in this way a too long osmosis of the solute and at the same time produce the necessary stretching of the membrane. After the indicated period of time the osmometer was immersed in water, and the determination of the maximum hydrostatic pressure could begin at once. The results are given in Table I, where C is the concentration of sodium chloride immediately after the determination of the maximum pressure expressed in g-mol in a liter, P is osmotic pressure corresponding to this concentration and P_m is the maximum hydrostatic pressure in the osmometer, both expressed in cm. of water column.

TABLE I

Maximum Hydrostatic Pressure P_m as compared to Osmotic Pressure.
Sodium Chloride. Parchment Paper

C	0.475	0.290	0.177	0.135	0.088
P_m	502	367	278	233	144
P	20910	13050	8120	6240	4110
P_m/P	0.024	0.028	0.034	0.036	0.035
C	0.067	0.050	0.029	0.026	0.016
P_m	122	97	62	59	39
P	3150	2370	1390	1250	770
P_m/P	0.035	0.040	0.045	0.047	0.050

From the results cited above we may conclude that the ratio P_m/P is approximately constant at the concentrations ranging from about 0.06 to 0.3 g-mol, but increases with a further decrease of the concentration. This may show that the permeability of parchment paper is constant at middle concentrations, but changes at the extremes.

In the experiments just described the membrane of parchment paper used was an old one, that is, it was used for filtration of water and salt solutions for three months. Such a filtration increases the permeability of parchment paper to water as well as to sodium chloride. The data concerning a fresh membrane of the same parchment paper will be revealed later.

Determination of Permeability Factors

In order to determine the permeability factors μ and σ the maximum hydrostatic pressure was determined for an ordinary membrane of parchment paper and for a double layer membrane of the same paper. The latter was made of two sheets of parchment paper stuck together with potato starch paste. The membranes were used for a filtration of water only for some days. After the maximum hydrostatic pressure in the osmometer had been determined, the same osmometer was used for the determination of the filtration rate of water and for the estimation of constants of the diffusion of sodium chloride through the membranes. The former, divided by the pressure used for the filtration gives the permeability of the membranes to water, while the diffusion constant gives the permeability of the latter to sodium chloride.

After the maximum hydrostatic pressure was determined, using one of the above membranes, the osmometer was filled with the solution of sodium chloride of a similar concentration but it was not connected with the capillary tube: it was closed with a rubber stopper through one of whose two openings a stirrer was introduced into the osmometer, while through the second opening a graduated glass tube was inserted bent horizontally in its outer part. This tube served for measuring of the volume of water sucked into the osmometer during the experiment. After a period of time indicated in tables during which the osmometer was immersed in the water of the bath the concentration of the solution in the osmometer was determined again. The concentration changes not only because sodium chloride diffuses through the membrane but also because water is sucked into the osmometer, and the concentration found by titration should be therefore corrected. The volume of the osmometer was 289 cc. If n cc of water were sucked into the osmometer, the corrected concentration is $1 + n/289$ times greater than the found one. The diffusion of sodium chloride through the membrane proceeded directly in the water of the thermostat bath. The volume of the latter was 170 times greater than that of the osmometer, the water in both was continuously stirred, and the concentration of sodium chloride in the bath at the end of experiments was not greater than 0.005 g-mol in a liter. Thus, this concentration was simply subtracted from the final concentration of sodium chloride in the osmometer. The diffusion constant K was calculated according to Fick's formula: $dS/dt = -KQ$ dC/dt , which in our case takes the form: $VdC/dt = -KQC$, where V is the

volume of the osmometer, C the changeable concentration of sodium chloride in the latter, t is time period, and Q is the area of the membrane. After the integration we have: $K = (\log C_0 - \log C)/Qt$ where C_0 is the initial concentration, C the final concentration of sodium chloride in the osmometer. K is expressed in tables in g-mol passing through one sq. cm. of the membrane in one hour. The maximum hydrostatic pressure in the osmometer was determined for each membrane for three concentrations of sodium chloride, while the diffusion constant was found for two middle concentrations. The results are given in Tables II and III.

Concerning the permeability of both membranes to water, it was determined in the following manner. The osmometer was washed, filled with water and connected with the capillary tube as it was done in the case of the determination of the maximum hydrostatic pressure, but the capillary tube was filled with water. Then the osmometer was immersed in the water of the thermostat bath and the pressure in it was raised to 100 cm of water column. After three days of the filtration of water through the membrane under this pressure the rate of filtration was determined. It was found that this rate expressed in cc of water passing through one sq. cm. of the membrane during one hour is for the ordinary membrane equal to 215×10^{-5} and for the double layer membrane to 115×10^{-5} . This result is in accord with the supposition that the filtration rate is inversely proportional to the membrane thickness (Manegold and Hofmann.⁷ The permeability of the membranes to water is accordingly 215×10^{-7} and 115×10^{-7} .

TABLE II

Maximum hydrostatic pressure P_m (cm of water column) as compared to osmotic pressure P . I for the ordinary membrane, II for the double layer membrane. C is the final concentration of sodium chloride in the osmometer (g-mol in a liter).

	I. Ordinary membrane			II. Double layer membrane		
C	0.124	0.071	0.035	0.122	0.072	0.033
P_m	111	60	39	218	120	81
P	5750	3340	1670	5650	3400	1580
P_m/P	0.019	0.018	0.023	0.039	0.035	0.051

TABLE III

Constant K of the diffusion of sodium chloride through the ordinary and double layer membrane. C_0 is the initial concentration, C is the corrected final concentration of sodium chloride. T is the time period during which the diffusion took place, in hours.

	I. Ordinary membrane		II. Double layer membrane	
C_0	0.1355	0.0629	0.1360	0.0705
C	0.1271	0.0589	0.1276	0.0636
T	2	2.03	4	6.73
K	0.0724	0.0720	0.0360	0.0345

⁷ E. Manegold and R. Hofmann: *Kolloid-Z.*, **49**, 372 (1929); **50**, 22 (1930).

From these results we may conclude that the decrease of the permeability of the membrane used to water and sodium chloride approximately two times brings about the increase of the hydrostatic pressure in the osmometer two

times. We may write, therefore: $2 = \frac{(1 - \frac{\mu}{2})(1 - \frac{2\mu}{2\sigma})}{(1 - \mu)(1 - \frac{\mu}{\sigma})}$ or $\mu = 0.66$. Con-

sidering now that the ratio P_m/P in the case of the ordinary membrane is equal at an average to 0.02 we may conclude that: $0.02 = 0.33 (1 - 0.67/\sigma)$, or $\sigma = 0.71$.

Test of the Formula

Comparing the data given in Tables I and II we may conclude that the ratio P_m/P in the case of the membrane used for the data of Table I is greater than that of the membrane used for the data of Table II. As it was mentioned before, the first membrane was an old one through which water and salt solutions were filtered for three months while the second membrane was fresh and used for filtration only for some days. The difference in the ratio P_m/P is evidently explained by the fact mentioned before that prolonged filtration increases the permeability of parchment paper to water and sodium chloride. It was interesting to find both permeabilities for the membrane of Table I and to calculate according to the so obtained data the ratio P_m/P which should be similar to the same ratio found by the experiments if the formula expressing the dependence of the maximum hydrostatic pressure upon the permeability is correct.

The data concerning the diffusion constant of sodium chloride are given in Table IV.

TABLE IV

Constant K of the diffusion of sodium chloride through the membrane of parchment paper through which water had been filtered during three months. C_0 the initial concentration, C the final concentration (g-mol). T is time period during which the diffusion took place.

C_0	0.1525	0.0970	0.0490	0.0258
C	0.1431	0.0895	0.0443	0.0222
T	1.5	2	2.48	3.17
K	0.0930	0.0910	0.0908	0.0801

We see therefore that the diffusion constant for the membrane of Table I is at an average 0.0887, while for the membrane of Table II this constant is 0.0722. In other words, a prolonged filtration increased the permeability of the membrane for sodium chloride 1.23 times. The permeability to water was found to be also increased. For the membrane of Table I it was found to be 310×10^{-7} while this permeability for the membrane of Table II is, as it was mentioned before, 215×10^{-7} , that is, 1.44 times smaller. The ratio P_m/P for

the membrane of Table I may be calculated therefore from the following equation:

$$P_m/P = (1 - 1.23 \mu) (1 - \frac{1.23 \mu}{1.44 \sigma}), \text{ where } \mu = 0.67 \text{ and } \sigma = 0.71 \text{ or } P_m/P = 0.034.$$

The found ratio is very near the ratio found by the experiments for the membrane of Table I. Namely, it is at an average 0.037 (see Table I).

We may conclude therefore that the formula expressing the dependence of maximum hydrostatic pressure upon the permeability of a membrane found theoretically is confirmed by these experiments.

In order to test the formula for different concentrations of sodium chloride at which the ratio P_m/P was found to be different the membrane of Table I was used not only for the determination of the diffusion constant but also of the permeability to water at different concentrations of sodium chloride, Brukner⁸ observed an increase of the filtration rate by addition of sodium chloride to water while the increase produced by weaker concentrations was found to be greater than that produced by strong concentrations. In the present experiments the osmometer was placed in a metal box covered inside with wet filter paper to prevent evaporation from the surface of the membrane, and after it was filled with a solution of sodium chloride the filtration rate was determined. It was found that, indeed, the filtration rate was greater than that in the case when water was filtered through the membrane, but between 0.04 and 0.15 g-mol it does not vary distinctly. We may assume therefore that it is constant at this concentration range. At concentrations which were lower than 0.04 g-mol the permeability decreased, however by about ten percent. In Table V are given the results. In this table C is the concentration of sodium chloride (g-mol), P is osmotic pressure in cm. of water column, K is diffusion constant, P_m is the maximum hydrostatic pressure experimentally found, P_m' the same pressure but calculated according to the formula $P_m = P (1 - \mu)(1 - \mu/\sigma)$ where μ is supposed to be proportional to K, and σ is proportional to the permeability of the membrane to water at different concentrations. As it was found above at concentrations ranging from 0.07 to 0.08 g-mol μ is equal to 0.82 and σ is equal to 1.02.

TABLE V

Maximum Hydrostatic Pressure experimentally found and calculated

C	P	K	μ	P_m (exp. f.)	P_m' (calc.)
0.159	7310	0.093	0.84	254	206
0.106	4930	0.092	0.83	179	155
0.071	3320	0.091	0.82	119	117
0.053	2520	0.091	0.82	95	89
0.029	1390	0.082	0.74	62	52

Considering the fact that μ and σ in the above formula were calculated approximately we may conclude from the results cited that this formula is confirmed by the experiments in a satisfactory degree.

⁸ Brukner: Z. Ver. deutsch. Zuckerind., 72, 3 (1926).

Outlook on the Further Application of the Formula

In the experiments presented in the preceding chapters one and the same sort of parchment paper was used for the membrane. One can not doubt that it will be found correct also for other membranes. It should be emphasized, however, that μ and σ in the formula expressing the dependence of the hydrostatic pressure in the osmometer upon the permeability of the membrane should be determined for every membrane separately because the coefficients of proportionality between them and the permeability can be expected to be different. Some experiments made on two different sorts of parchment paper showed, for instance, that the diffusion coefficient of sodium chloride can be three to four times greater than in the case of parchment used in the experiments described above. It is evident that μ for these sorts of parchment paper can not be three or four times greater than it was found in these experiments. Otherwise the osmotic force of the membranes would be a negative value which is impossible.

On the other hand, the ratio μ/σ was near one for the membrane of parchment paper used in these experiments, because the exosmosis of sodium chloride from the osmometer into water expressed in grams through 1 sq. cm. was about one to one and a half times less than the endosmosis of water into the osmometer. If this ratio decreases, the hydrostatic pressure in the osmometer increases, and if the permeability of a membrane to water is very great in comparison with that to solute, the formula is practically transformed to: $P_m = P(1 - \mu)$. Such a case is evidently observed on the precipitation membrane of copper ferricyanide. Indeed, Tammann's experiments showed that the values μ calculated from Pfeffer's experiments in supposition that $P_m = P(1 - \mu)$ is proportional to the constant of the diffusion through this membrane.⁹ The same case is also observed on living protoplasm which moreover possess a very small permeability factor μ so that the osmotic pressure which develops inside of the cells is near the theoretic value of osmotic pressure.

Summary

1. A too low hydrostatic pressure observed in an osmometer in which parchment paper is used as a membrane is not due to an accumulation of the solute (sodium chloride) under the membrane. The pressure which is about thirty times smaller than the theoretic osmotic pressure corresponding to the concentration of sodium chloride in the osmometer is increased very little when a water current giving 12 liters in one minute is directed on the membrane from below.

2. The force with which a membrane sucks water into an osmometer depends upon the permeability of the membrane to solute (sodium chloride). This dependence can be expressed by the formula $P_o = P(1 - \mu)$ where P_o is the *suction force of the solution*, P is its osmotic pressure and μ is the permeability factor proportional to the permeability of the membrane to solute.

⁹ Here μ is substituted for γ/nv of his formula.

3. The maximum hydrostatic pressure in the osmometer depends in general not only upon the permeability of a membrane to solute but also to its permeability to water. This dependence can be expressed by the formula: $P_m = P(1 - \mu)(1 - \mu/\sigma)$ where P_m is the maximum hydrostatic pressure, and σ is the permeability factor proportional to the permeability of the membrane to water. In the case of a copper-ferricyanide membrane the formula of paragraph 2 is practically valid for the maximum hydrostatic pressure in the osmometer because the permeability to water is much greater in this case than the permeability to the solute (Tammann).

4. The factor of permeability as calculated from the experiments described in this paper for one kind of parchment paper and sodium chloride are equal: $\mu = 0.67$ and $\sigma = 0.71$. If the same parchment paper was used for filtration of water and salt solutions during three months, these factors became $\mu = 0.83$ and $\sigma = 1.02$.

AN UNUSUAL CRYSTAL GROWTH¹

BY H. G. TANNER

A very peculiar crystal growth was observed when an attempt was being made to coordinate aniline with aluminum nitrate. Nineteen grams of aluminum nitrate nonahydrate (0.05 mole) was dissolved in sixty cc. of methanol. The solution was cooled with ice water, and to it was added with

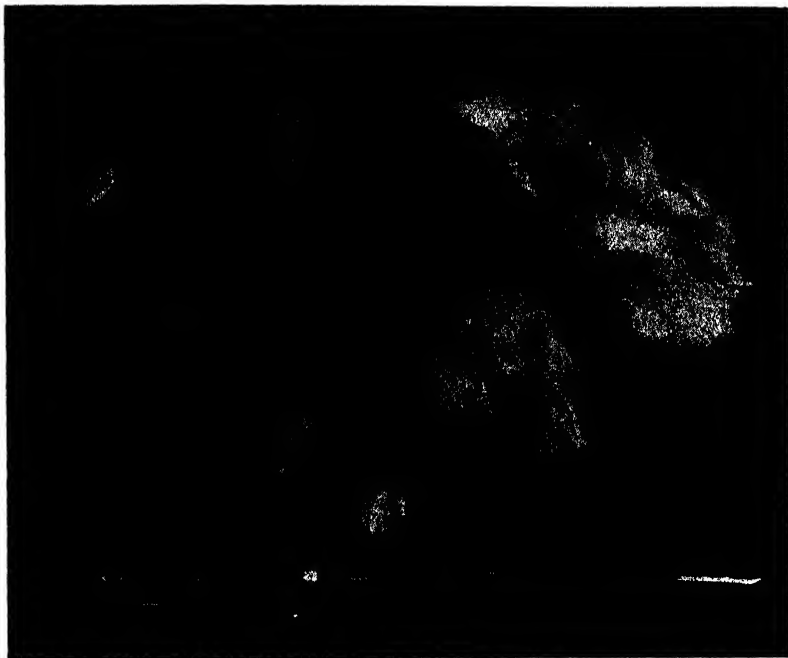


FIG. 1

stirring fourteen grams of aniline (0.15 mole). A gel was formed which underwent partial syneresis rapidly. The initial exudate was removed by filtration on a Buchner. The gel was transferred with minimum disturbance to a piece of paper, and exposed to the air. From the gel grew a large tuft of white, lustrous, hair-like crystals shown by the accompanying photograph. The growth continued over a period of twenty-four hours. In one experiment the crystals attained a length of twenty-five centimeters.

The crystals were analyzed and found to be aniline nitrate containing a trace of aluminum. The aluminum was present as a mechanical occlusion rather than a chemical constituent of the crystals.

¹ Contribution No. 101 from the Experimental Station, E. I. du Pont de Nemours & Co.

Gels prepared with double the proportion of aniline behaved similarly, but a smaller quantity of aniline stunted the crystal growth. With the exception of ferric nitrate, no other salt was found to behave with aniline as did the aluminum nitrate.

The gel, as prepared by the above described procedure, was translucent because of the numerous bubbles and cracks developed by the agitation and filtration. This condition favors the formation of a larger "flower" of crystals, but renders difficult the microscopic observation of the mechanism which operates to form this peculiar type of growth. For the latter purpose a gel was prepared in a slightly different manner. The solution of aluminum nitrate was prepared as before, but cooled to -25° before adding the aniline. The low temperature permitted mixing of the aniline with the salt solution without apparent reaction. After the aniline had been added, the mixture was allowed to warm up to room temperature. Upon standing a few minutes it set to a nearly clear gel. Alcohol evaporated, of course, from the surface of this gel, and tiny crystals of aniline nitrate made their appearance. These were watched with a low-power microscope. They did not grow continuously, as would be expected, but spasmodically. When a crystal attained a certain size, which differed for individual crystals, the gel suddenly shrank away from the sides of the crystal. Any further growth therefore had to occur on the bottom face. In some manner, not understood, growth on the bottom forced the crystal upward. A height of six or seven centimeters above the surface of the gel was frequently attained by these crystals.

BERYLLIUM

IV. Micro Qualitative Analysis of Beryllium*

BY HAROLD SIMMONS BOOTH AND SPENCER GUILD FRARY

Introduction

Beryllium, although discovered in 1793 by Vauquelin and first prepared by Wöhler in 1828, has not shown much possibility of commercial importance until quite recently. However the demands of industry for light, strong alloys for aircraft and highly specialized alloys for other purposes will probably increase manufacturing of the metal and bring the price down to the point where it can be profitably employed.²²

Beryllium is not a rare element and in certain localities is rather abundant. Washington²⁵ states that "beryllia has never, so far as I know, been determined in the analysis of an igneous rock. Yet the fact that the aluminosilicate, beryl, is not a rare mineral indicates that beryllium is fairly widespread. Beryl occurs in granitic and syenitic pegmatites, especially sodic ones. It is also found in metamorphic rocks. It has been suggested that in some cases beryllia has been weighed with, and supposed to be alumina, unidentified beryl being present, thus accounting for an apparent excess of Al_2O_3 , which it is difficult to reconcile with the mineral composition of the rock. It has been shown recently that alumina has been mistaken for beryllia in the mineral vesuvianite,²⁰ in which the presence of beryllium had not been suspected. The need of a closer study of some minerals and rocks as regards this point is obvious. It might be well to determine BeO in granites associated with beryl-bearing pegmatites and in some nephelite syenites."

In a more recent article Washington²⁴ again stresses the importance of analyzing silicate minerals and igneous rocks for beryllium. Berylite was found to contain beryllium in place of the aluminum hitherto supposed to be present.

Because of its low atomic weight the percentage of beryllium in most minerals is not very great; beryl, the most common, contains only 4 to 5 per cent beryllium as the metal. Since beryl is the present commercial source of the element despite a hardness of 7.5 to 8 and the natural difficulty of decomposing silicates which make it far from satisfactory, it is of interest to know if there are other sources of the element that might prove of value.

To prevent the element from being overlooked in the future it is important that the methods of its detection be improved, if possible. To this end a study of the microqualitative detection of beryllium has been made.

* Contribution from the Morley Chemical Laboratory, Western Reserve University. For Beryllium I, II, and III see *J. Phys. Chem.*, **35**, 2465, 2492, 3111 (1931).

Historical

Beryllium at the head of group II of the periodic table has many of the chemical characteristics of aluminum in group III. The two hydroxides closely resemble each other and it is their separation that offers the chief difficulty in quantitative analysis. In the ordinary course of analysis they are precipitated together and weighed as alumina.

There have been many separations suggested for beryllium and aluminum. Of these methods, Britton² found that the best were:

1. Decomposition of sodium beryllate solutions by boiling to precipitate beryllium hydroxide.¹¹
2. Parsons and Barnes' method of momentarily boiling a saturated solution of sodium bicarbonate.²¹
3. Wunder and Wenger's method of fusing the oxides of beryllium and aluminum in sodium carbonate. Sodium aluminate is formed while the beryllia is unaffected.²⁶
4. Haven's method in which a concentrated solution of the chlorides is treated with an equal volume of ether and dry hydrogen chloride gas passed in, to precipitate the aluminum chloride.¹²

Since that time a newer separation in which 8-hydroxyquinoline is used to precipitate the aluminum has been developed which is quite satisfactory for quantitative analysis.^{16,17}

For the determination of small amounts of beryllium in large amounts of aluminum, a combination of the Havens, and 8-hydroxyquinoline methods has been suggested.⁷ By this means most of the aluminum is removed first, avoiding the use of an excessive amount of the rather expensive 8-hydroxyquinoline.

In the analysis of minerals, Hills¹⁴ recommends the use of Parsons' method of boiling a concentrated solution of sodium bicarbonate, followed by the 8-hydroxyquinoline separation to remove the last of the aluminum.

There are very few really distinctive qualitative tests for the detection of either beryllium or aluminum. H. Fischer⁹ suggests the use of quinalizarin (1,2,3,8 tetrahydroxy anthraquinone alizarin bordeaux) for the detection of small amounts of beryllium and I. M. Kolthoff¹⁵ suggests curcumin for the detection of the element. Both of these are adsorbed by beryllium hydroxide, giving characteristic colors.¹⁸

Microqualitative Methods of Analysis

Chemical microscopy, on the other hand, offers simple, easy methods of qualitative analysis in many cases where the ordinary methods are laborious and often inexact. In the case of beryllium there are several tests that distinguish it quite definitely from aluminum and other elements with which it might be associated.

A satisfactory microqualitative test should have the following characteristics: (1) the resulting product should have a large molecular weight in proportion to the amount of the element actually present; (2) a small amount of

the substance should give a positive test; (3) the products formed should have characteristics that distinguish them from the reagent and from any other elements that might be present; (4) the test should give good results under not too rigid conditions; (5) the test should be comparatively simple and not involve too many steps; (6) the resulting products should have an index of refraction so different from the solution that they may be easily distinguished.

Double salts of beryllium should give good tests because of the low atomic weight of the element. For example, in the potassium oxalate test the double salt formed has a molecular weight of 263, of which only 9 parts are due to the beryllium present. Likewise in the chloroplatinic acid test the crystals obtained have the composition $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$, with a molecular weight of 560, only 9 parts of which are due to the element being detected.

The third requirement, that of characteristic properties of the products, is not so well met in the case of beryllium, due to the fact that so many of the insoluble compounds of beryllium separate as amorphous, basic salts that have no distinguishing characteristics. Since solutions of beryllium salts have the property of dissolving beryllium hydroxide and the salts also hydrolyze quite readily, it is, in many cases, difficult to get crystalline products of definite composition. This property probably accounts for many of the strange, unsubstantiated compounds found in the literature of beryllium.

Many reagents cause the precipitation of the hydroxide which in itself is useless as a microqualitative test for beryllium; though failure to obtain any hydroxide precipitate can be taken as a negative test showing the absence of the element. Or the precipitate can be filtered and dissolved in a small amount of acid thus concentrating it and increasing the accuracy of the test as well as effecting a separation from other material that might interfere.

Precipitation with ammonia and filtration through a microfilter, or careful evaporation of the test drop, will show amounts of the hydroxide down to 0.0007 mg. With smaller amounts a spectrographic analysis is the best means for the detection of beryllium.

Experimental

To determine the limit of accuracy of the various methods a procedure similar to that given by Chamot and Cole was used.⁵ A series of four beryllium nitrate solutions were made up such that each was one-tenth the concentration of the previous one.

In order to be sure of getting the same amount of solution each time, micropipettes made by drawing out glass tubing to a capillary tip and attaching rubber bulbs to facilitate handling the solutions, were used. Measurements into a graduated cylinder showed the drops to average fifty to a cubic centimeter hence each contained 0.02 cc.

Gravimetric analysis of the first solution showed it to contain 3.3 mg. of beryllium per cubic centimeter, or 0.066 mg. per drop. The beryllium content per drop of the different solutions was:

No. 1	0.066 mg. beryllium per drop
No. 2	0.0066 mg. per drop
No. 3	0.00066 mg. per drop
No. 4	0.000066 mg. per drop

Most limits of accuracy are given in micro milligrams (μ mg.), equivalent to 0.001 mg. Expressed in this manner the four solutions would have the following beryllium content per drop: No. 1, 66.0μ mg.; No. 2, 6.6μ mg.; No. 3, 0.66μ mg. and No. 4, 0.066μ mg.

The textbooks on chemical microscopy^{6,17,1} give the following methods for the detection of beryllium:

1. Reaction with potassium oxalate to form the double salt, beryllium potassium oxalate ($K_2C_2O_4 \cdot BeC_2O_4$).
2. Reaction with chloroplatinic acid to form beryllium chloroplatinate, ($BePtCl_6 \cdot 8H_2O$).
3. Reaction with sodium and uranyl acetates to form the triple salt, sodium uranyl acetate, $Na(C_2H_3O_2) \cdot Be(C_2H_3O_2)_2 \cdot 3UO(C_2H_3O_2)_2 \cdot 9H_2O$.

All three of these books recommend the potassium oxalate method as the best for beryllium.

Beryllium Potassium Oxalate. $K_2C_2O_4 \cdot BeC_2O_4$.

Chamot⁶ recommends a neutral, moderately concentrated test drop to which a little acetic acid is added; then the reagent is added in a fragment that, in this case, must be more than twice the size ordinarily used.

According to Chamot, " $K_2C_2O_4 \cdot BeC_2O_4$ separates in large, stout, clear, colorless, monoclinic prisms; single, in twins, or in groups of radiating, irregularly formed prisms. Thin plates in the form of rhombs are also obtained. The salt is strongly birefringent and exhibits an extinction angle of about 39° .

"Unless the reagent is present in sufficient excess the test is apt to prove unsatisfactory. Acid potassium oxalate or the oxalates of sodium or ammonium are not suitable reagents.

"During the disintegration and solution of the reagent fragment well-formed crystals of $K_2C_2O_4$ usually appear momentarily. These crystals often bear a striking resemblance to the double salt, and it is therefore imperative that the analyst shall be on his guard lest he fall into error through too hasty a decision."

Chamot adds that the double salt can be recrystallized by gently warming the slide and cooling, whereupon well-formed crystals are obtained.

Behrens¹ suggests the addition of a little mercuric chloride to cause the formation of elongated prisms, thus making it easier to distinguish the double salt from the reagent.

Lindsley¹⁷ states that ammonium salts should be absent when testing for beryllium with potassium oxalate.

When this test was made according to Chamot⁶ crystals were obtained with all the solutions. It was subsequently found that acetic acid in a drop of water gave similar crystals. Solutions of beryllium salts hydrolyze suf-

ficiently to give the slight acidity necessary for the formation of the double salt so that the addition of acetic acid is unnecessary and should be avoided as it interferes with the test.

Behrens¹ gives 0.08 mg. as the limit of accuracy of the potassium oxalate method. This is the minimum amount of beryllium in a test drop that will give a positive test. This would correspond to slightly more than one drop of the No. 4 solution.

A positive test was obtained with the No. 3 solution equivalent to a limit of accuracy of 0.7μ mg.

Before arriving at these conclusions, several methods of obtaining the right acidity and at the same time avoiding ammonium salts were attempted. It was found, however, that ammonium salts did not interfere and that beryllium hydroxide, dissolved in a little hydrochloric or sulfuric acid, or solutions of the salts, could be used for the test without any preliminary treatment.

Very dilute solutions can be concentrated by gentle evaporation and highly acidic solutions had best be neutralized with ammonia and the precipitated hydroxide dissolved in acid.

Aluminum, ferric iron and chromium gave no crystals with the reagent. They are the elements most likely to be present in the ordinary course of analysis.

Adding mercuric chloride to the solution made no appreciable change in the shape of the crystals obtained and appeared to interfere with the test to some extent.

Beryllium Chloroplatinate, $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$.

This test is performed by evaporating the test drop to a nearly dry film and then drawing the concentrated reagent solution across the film in a narrow channel. Beryllium chloroplatinate separates out in hygroscopic, faintly yellow, square and rectangular plates, usually singly, but sometimes penetration twins are formed. Chamot⁶ says that the formation of the crystals can be induced by the addition of alcohol.

The precipitate should be examined with crossed nicols. The beryllium salt exhibits parallel extinction and is only weakly birefringent. As the alkali metals form characteristic crystals with chloroplatinic acid they should not be present in too great amounts.

Chamot states further that in his opinion this test is valueless unless the material is so high in beryllium as to constitute a fairly pure salt.

When this test was first tried no crystals were obtained due to the reagent solution being too dilute; after evaporating it down to a thick sirup good results were obtained with the No. 3 solution. Therefore, the limit of accuracy was found to be 0.7μ mg.

However, the addition of alcohol recommended by Chamot caused everything to dissolve and spoiled all the crystals rather than aiding in their formation.

Aluminum did not interfere with this test and it is probable that, if the beryllium and aluminum were precipitated as the hydroxides and washed free from everything else, except possibly a slight trace of ammonium salts, this test would work reasonably well.

Sodium Beryllium Uranyl Acetate.

Beryllium is supposed to form a triple salt with sodium and uranyl acetates similar to those formed by magnesium and zinc. This method is mentioned by Caglioti³ as a test for beryllium but neither Miholic¹⁹ nor Bedient⁴ were able to obtain the triple acetate unless the solution went to dryness.

When this test was tried no crystals were obtained that could be used as a test for beryllium. It seemed impossible to get the salts to crystallize unless the solution was evaporated almost to dryness.

Caglioti³ also suggests the acetyl acetone derivative prepared by treating acetyl acetone with beryllium acetate solution, slightly acidified with acetic acid. Monoclinic tablets, or thin prisms, are supposed to be obtained by slow crystallization. Caglioti states that this is preferable to the triple acetate as a microqualitative test for beryllium.

This test recommended by Caglioti was also attempted but no crystals were obtained. On one occasion some crystals were observed but, on repeating the test under apparently the same conditions the crystals failed to reappear.

Search for New Reagents

With the hope of finding a reagent better than potassium oxalate for the microqualitative analysis of beryllium, many substances which give distinctive tests, with other elements, were tried with beryllium salts.

Since the great majority of these failed to give any definite reactions with beryllium the results are only briefly given in tabular form.

TABLE I

Reactions of several organic compounds with beryllium nitrate solutions, first alone, then with KCNS, and finally with KCNS in acid solution were investigated, and also those with aluminum chloride were tried to determine what effect it would have as an impurity.

Reagent	Beryllium nitrate	Aluminum Chloride
Acridine	No action alone. Reacted with KCNS to give crystals	No action
Resorcine	No action	No action
Benzidine	No action; crystals of reagent on heating	No action
Diphenylamine	No action	No action
Phthalic anhydride	No action	No action
Picric acid	No action; crystals of reagent on heating	No action
Pyrogallie acid	No action; crystals of reagent on heating	No action
Uric acid	Reagent insoluble; no action	No action
Eosine	No action	No action
Fluorescene	No action	No action

TABLE II

Results of reactions of inorganic compounds on solutions of beryllium nitrate.

Potassium dichromate	No reaction
Potassium permanganate	No reaction
Potassium tartrate	No reaction
Potassium antimonate	Precipitated beryllium hydroxide
Sodium arsenate	Precipitated beryllium hydroxide
Sodium bismuthate	Precipitated beryllium hydroxide
Sodium nitrate	No reaction
Sodium phosphotungstate	White curdy precipitate
Sodium nitroprusside	No reaction
Sodium thiosulfate	No reaction
Disodium phosphate	White curdy precipitate
Ammonium persulfate	White curdy precipitate
Ammonium phosphomolybdate	Only soluble in alkaline solutions; beryllium hydroxide precipitates
Dimethylglyoxime	No reaction
Ammonium vanadate	Orange color and precipitate. (Aluminum gave a pale yellow color)
Ammonium fluostannate	No reaction (aluminum gave a precipitate)
Ammonium fluotitanate	No reaction (aluminum gave a precipitate)
Potassium fluoride	No reaction (aluminum gave a precipitate)
Potassium bifluoride	No reaction (etched the slide rapidly).

TABLE III

Beryllium hydroxide was dissolved in solutions of the following acids and evaporated.

Succinic acid	No reaction
Citric acid	No reaction
Tartaric acid	No reaction
Malonic acid	No reaction
Salicylic acid	No reaction
Cinnamic acid	Rectangular crystals
Benzoic acid	Needle crystals

The majority of the substances studied gave no particular reaction but there were a few that appeared to have interesting possibilities, that deserve a more detailed discussion.

The reaction of sodium fluoride and some of the fluo-salts with solutions of beryllium and aluminum salts is a means of distinguishing between them and has been proposed as a method of separation.¹⁰

Britton² states that this method is not quite quantitative due to the slight solubility of sodium aluminum fluoride. However, a sample of beryllium oxide made by the Copaux⁸ process in which the separation is based on

the insolubility of the sodium aluminum fluoride, showed little if any aluminum when examined spectrographically.

However, the use of fluorides under the microscope is rather objectionable as special precautions have to be observed to protect the lenses from corrosive fumes. Cover glasses can be fastened to the objective with cedarwood or Canada balsam, but even so there is danger of corrosion if used for any length of time.

Test with Potassium Malonate

Potassium malonate was studied because malonic acid is the second member of the series of organic acids of which oxalic is the first. As the potassium oxalate test is the best so far known for beryllium, it was of interest to determine if potassium malonate would give a similar reaction with solutions of beryllium salts.

A fragment of the salt was added to the test drop and the solution carefully evaporated. With more concentrated solutions, well shaped rhombs were formed at the edge of the drop. When these were pushed into the center and the evaporation continued, long monoclinic prisms were formed.

The rhombs, observed under polarized light, with crossed nicols, gave oblique extinction at an angle of 38° . The prisms showed parallel extinction.

The rhombs were obtained in a drop of the No. 1 solution; the No. 2 solution gave only the prisms. The limit of accuracy of this method would be 6.6μ mg.

Test forming Beryllium Basic Acetate

Beryllium is unique in forming a volatile basic acetate. This compound is prepared²³ by dissolving the hydroxide in acetic acid, evaporating the solution to a gummy mass, dissolving in glacial acetic acid, and boiling off the excess acid; on cooling the solution, the basic acetate separates out in the form of octahedral crystals.

While this method is not easily applicable to tiny amounts of unknown, if about a cubic centimeter of unknown solution is taken and the beryllium converted to the basic acetate, only a small amount of the resulting solution need be taken.

Although the absolute accuracy of this test is in the order of one milligram, this is more than compensated by the fact that the crystals obtained are highly refractive and quite characteristic.

The glacial acetic acid is very mobile and it is best to place the drop to be observed in a hollowed-out slide to prevent its spreading over the slide and evaporating too rapidly.

TABLE IV

The limit of accuracy of these methods:

Beryllium potassium oxalate	0.7μ mg.
Beryllium chloroplatinate	0.7μ mg.
Beryllium malonate	7.0μ mg.
Beryllium basic acetate	1000μ mg

Conclusions

The most satisfactory microqualitative test for beryllium so far found is the potassium oxalate method. It does not require any elaborate procedure and the sensitivity is more than sufficient for all practical purposes. The limit of accuracy is about 0.7μ mg. Contrary to the literature, acetic acid should be avoided and ammonium salts do not interfere.

The chloroplatinic acid test is suitable where the beryllium is not too contaminated with other material. In some cases the beryllium and aluminum can be separated from other material as the hydroxides, before applying the test. With pure beryllium solutions the limit of accuracy of this test is 0.7μ mg.

Potassium malonate can be used as a reagent for the detection of beryllium. The limit of accuracy is 7.0μ mg.

Beryllium basic acetate recrystallized from acetic acid can be used as a confirmatory test for the element though its limit of accuracy is only about one milligram.

The reactions of the fluorides can be used as a means of distinguishing beryllium from aluminum provided precautions are taken to protect the apparatus from fluoride fumes.

The above methods of microqualitative analysis offer the best means for the detection of beryllium. They are superior to the ordinary methods of qualitative analysis both in simplicity and in accuracy. If these methods are applied to the precipitated hydroxides ordinarily obtained in macro qualitative analysis, they should show conclusively the presence of any hitherto unsuspected beryllium.

Summary

1. The application of the methods of chemical microscopy to the qualitative analysis of beryllium was studied.

2. A study was first made of the present method to determine their limitations and advantages.

The potassium oxalate method was found to be the most satisfactory.

The chloroplatinic acid method was found satisfactory under certain conditions.

3. An attempt was made to find new methods that would supplement or replace the present ones.

4. As a result of this investigation two methods are proposed:

The use of potassium malonate in a manner similar to potassium oxalate.

The use of the basic acetate recrystallized from glacial acetic acid as a confirmatory test.

5. The above micro methods are believed to be superior to the macro qualitative methods, as a means of identification of beryllium, especially if applied to the precipitate of aluminum and beryllium hydroxides, as ordinarily obtained in macro qualitative separations.

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NITROGEN COMPOUNDS OF GALLIUM

III. Gallic Nitride*

BY WARREN C. JOHNSON, JAMES B. PARSONS AND M. C. CREW

Introduction

A nitride of each member of Family B, Group III, of the periodic system with the exception of gallium has been reported in the literature. Boron nitride has been prepared by several different methods. Stock and Blix¹ obtained the nitride by the decomposition of boron imide; Meyer and Zappner² passed a mixture of boron trichloride and ammonia through a tube heated at high temperatures and obtained boron nitride of high purity; and Friederich and Sittig³ have reported the formation of the compound through the direct combination of its elements at 1200°. It is described by several workers as an exceedingly stable compound. Aluminium has been shown to combine directly with nitrogen⁴ to form a nitride of definite composition. The nitrides of indium and thallium have been reported by Fischer and Schroter.⁵ They employed the discharge of an electric arc through a mixture of liquid argon and liquid nitrogen, with the metal serving as electrodes, to cause combination of the elements. In each case a black powder was obtained which appeared to be quite unstable thermally, even at very low temperatures. The data available at the present time are not sufficient, however, to warrant the existence of indic and thallic nitrides as definite compounds. On the other hand, Franklin⁶ has been successful in the preparation of thalious nitride, Tl_3N , in liquid ammonia solution from thalious nitrate and potassium amide.

In view of the position of gallium in third group of elements, one would predict the formation of a nitride possessing properties similar to those of the nitrides of aluminium and indium. The following report shows that gallic nitride resembles aluminium nitride and boron nitride in its apparent stability towards heat, solutions of acids and of bases.

Experimental

Metallic gallium was obtained from germanite ore according to a procedure previously described.⁷ It was purified by fractional crystallization on a platinum wire from the supercooled liquid metal.⁸ Liquid ammonia was thoroughly dried with sodium before being used in any of the experiments.

* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

¹ Stock and Blix: *Ber.*, **34**, 3039 (1901).

² Meyer and Zappner: *Ber.*, **54**, 560 (1921).

³ Friederich and Sittig: *Z. anorg. Chem.*, **143**, 293 (1925).

⁴ Fichter and Spengel: *Z. anorg. Chem.*, **82**, 192 (1913).

⁵ Fischer and Schroter: *Ber.*, **43**, 1465 (1910).

⁶ Franklin: *J. Phys. Chem.*, **16**, 682 (1912).

⁷ See Johnson and Parsons: *J. Phys. Chem.*, **34**, 1210 (1930) for brief description of method and other references.

⁸ Richards and Boyer: *J. Am. Chem. Soc.*, **43**, 274 (1921).

Gallium nitride, GaN, was prepared by the action of ammonia gas on metallic gallium at high temperatures. A boat containing the metal was inserted in a Vitreosil tube which was heated by an electric furnace. The temperature was measured with a Pt,Pt-Rh thermocouple and a Leeds and Northrup Potentiometer Indicator. Reaction was found to proceed slowly at a temperature as low as 700°, but it was necessary to heat the metal to 900-1000° for several hours in order to obtain an amount of the nitride sufficient for analysis and study. This procedure was found to be disadvantageous in two respects; (1) metallic gallium is appreciably volatile at temperatures approaching 1000° and consequently distills out of the boat to condense in the cooler regions of the tube without reacting with the ammonia, and (2) the nitride also sublimates at these temperatures to leave the reaction mass. However, the higher temperatures were employed throughout the preparations to obtain appreciable quantities of the nitride although it was found impossible to determine the extent of a given reaction merely by the change in weight of the boat and contents.

When the reaction between metallic gallium and ammonia was completed, the product was analyzed for nitrogen by the distillation of ammonia from a concentrated NaOH solution. The results are shown in Table I under samples listed (1) and (2) which represent two different preparations of the compound. The nitrogen content obtained from the analyses suggests that one atom of gallium is in combination with one atom of nitrogen. The reaction may be expressed as follows:

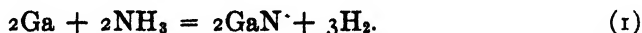


TABLE I

Analysis of Gallic Nitride for Gallium and Nitrogen

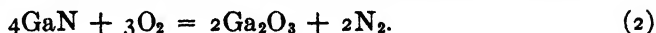
Sample	GaN, g.	Ga (found), g.	Ga (calcd.), g.	N ₂ (found), g.	N ₂ (calcd.), g
(1)	0.0689			0.0115	0.0115
(2)	.1802			.0299	.0301
(3)	.1207			.0209	.0202
(4)	.2070	0.1710	0.1724		
(5)	.2088	0.1746	0.1747		

In order to carry out an analysis of the nitride for nitrogen by the Kjeldahl method, concentrated NaOH solution was used to dissolve the compound. Dilute alkali appeared to have little effect on the nitride, and even the concentrated solution dissolved it slowly on heating. Attempts to recover the gallium from the solution, after the ammonia had been liberated, did not produce satisfactory results due to the presence of appreciable amounts of silica which had been removed from the glass. The possibility of reduction of the nitride at high temperatures with hydrogen to metallic gallium and ammonia was considered in view of the results previously obtained with germanic nitride.⁹

⁹ Johnson: J. Am. Chem. Soc., 52, 5160 (1930).

A small sample of the nitride, 0.1592 g, was heated in a stream of hydrogen at 800° for 24 hours. An examination of the material at the end of this period showed no change in its appearance but a loss in weight of 0.0385 g was noted. On the other hand, a considerable quantity of a grey substance resembling the nitride collected on the walls of the quartz tube outside the heated area. If the nitride were to be completely reduced to metallic gallium without any distillation, the loss in weight would be only 0.0266 g to correspond to the nitrogen. Accordingly, the material remaining in the boat was analyzed for nitrogen by the method indicated above. The results given in Table I (sample 3) show the material to be identical with gallic nitride. This conclusion is substantiated by the fact that the gases discharged from the reaction tube failed to produce any effect on a dilute HCl solution. Evidently, the nitride is slightly volatile at 800°, under a pressure of 1 atmos. of hydrogen, without suffering decomposition or reduction.

Two different methods were found applicable for the determination of gallium. In the first method, the nitride was dissolved in hot, concentrated H₂SO₄, the excess acid was evaporated, the residue dissolved in water, and the gallium was precipitated as hydroxide in the presence of NH₄HSO₃ according to the procedure described by Porter and Browning.¹⁰ The hydroxide was ignited and finally weighed as Ga₂O₃. The gallium content is calculated and shown in Table I (sample 4).¹¹ The second method for the determination of gallium was accomplished by passing oxygen gas over the nitride at high temperatures to form gallic oxide according to the following expression:



The oxidation was found to proceed slowly even at temperatures approaching 900°. At 500° no reaction was observed while at 800° some gallic oxide was noticed after several hours heating. Approximately 30 hours at 875-900° were required to completely oxidize a 0.2 g sample of the nitride. Sublimation of the nitride was not noticed in this experiment; undoubtedly, the oxide which forms at the surface tends to prevent an escape of the more volatile material. The results of the oxidation are given in Table I (sample 5).

All attempts to react metallic gallium directly with nitrogen gas were unsuccessful. Nitrogen was passed over the metal at temperatures ranging from 500-1000° for several days but no indication of a combination of the two constituents was observed.¹²

Properties of Gallic Nitride. Gallic nitride is an exceedingly stable compound. Above 800° it sublimates without decomposition. It is not reduced with

¹⁰ Porter and Browning: J. Am. Chem. Soc., **41**, 1491 (1919).

¹¹ No attempt was made here to determine the nitrogen of the nitride digested with the concentrated H₂SO₄. Undoubtedly, this procedure would allow for analysis of both nitrogen and gallium and thus eliminate the use of concentrated NaOH for the determination of nitrogen.

¹² Observations by Miss E. DeSylvester in this laboratory. Some gallic oxide was formed in this experiment due to traces of oxygen with the nitrogen which escaped removal in being passed over copper at 600°. However, the contents of the reaction chamber failed to show the presence of nitrogen when subjected to analysis.

hydrogen at 900° , but reacts slowly with oxygen at this temperature to form gallic oxide. The nitride is unchanged when treated with dilute and concentrated solutions of HCl, HF and HNO_3 . Hot aqua regia has no effect on the nitride. The compound dissolves slowly in hot, concentrated H_2SO_4 and also in hot, concentrated NaOH. It is stable in air; a sample exposed to air for several weeks showed no change in weight or in appearance. The nitride, as prepared by the reaction between metallic gallium and ammonia gas at high temperatures, appears as a dark grey powder.

Summary

Gallic nitride, GaN , is prepared by reacting metallic gallium with ammonia gas at $900\text{--}1000^{\circ}$. Some of its properties are studied and discussed.

Chicago, Illinois.

THE INFLUENCE OF GASES ON THE NORMAL POTENTIAL OF THE ZINC ELECTRODE

BY FREDERICK H. GETMAN

In all modern precise determinations of normal electrode potentials it is customary to exclude air from the electrolyte and the electrode vessel. Hydrogen and nitrogen are the two gases most commonly employed for this purpose. In a recent study of the effect of different gases on the potential of the aluminium electrode, Kahlenberg and French¹ have shown that oxygen, hydrogen and nitrogen produce marked changes in the potential of the metal as measured in air-saturated solutions of potassium chloride. Both nitrogen and hydrogen were found to render the potential decidedly more basic, whereas with oxygen the potential was found to be less basic than when air alone was present. In a subsequent communication the same authors² studied the effect of carbon monoxide, methane and helium, in addition to the gases previously mentioned, on the potentials of a number of metals and concluded that the metals form "gas-metal" electrodes with gases, the potentials being specific for each particular metal and gas, and related to the absorbing power of the metal for the gas, and the affinity of the metal for each gas in the case of a mixture. The total combined potential is believed to be due both to absorbed gas and a condensed film of the gas on the surface of the metal. Those elements which have a tendency to form acids behave differently with oxygen than do the other elements. Amphoteric elements as well as those which exhibit variable valence, or function as catalysts, were found to show greater changes with hydrogen and nitrogen than do the more pronouncedly metallic elements.

Both methane and carbon monoxide were shown to produce very appreciable changes in the potentials of both platinum and palladium. Coating the electrodes with collodion, or stirring the electrolyte, prevented the condensation of a gas film on the surfaces of the electrodes. It was found that those electrodes which exhibited the smallest differences between their oxygen and nitrogen potentials were in every case the most constant. The authors concluded that the so-called single potentials of the metals, determined in air, are in reality "air-metal" electrodes, and consequently that the commonly accepted electrochemical series of the metals requires fundamental revision. Whereas in the foregoing investigations the authors had confined themselves to a single electrolyte, normal potassium chloride, in a continuation of the investigation by Kreuger and Kahlenberg,³ the effects of oxygen, hydrogen, nitrogen, helium and argon on the potentials of all the common

¹ Kahlenberg and French: *Trans. Am. Electrochem. Soc.*, **52**, 355 (1927).

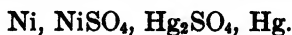
² French and Kahlenberg: *Trans. Am. Electrochem. Soc.*, **54**, 163 (1928).

³ Krueger and Kahlenberg: *Trans. Am. Electrochem. Soc.*, **58**, 107 (1930).

metals and carbon were studied in normal solutions of potassium chloride, potassium hydroxide and hydrochloric acid. It was found that the potentials of arsenic, natural graphite, coconut charcoal, cadmium, mercury, molybdenum, lead, silicon, tin, tantalum, tellurium, tungsten and zinc were only slightly altered by any of the gases, irrespective of which of the three electrolytes were used. The experimental data were interpreted as indicating that there is no such thing as a true gas electrode but that the so-called gas electrodes are to be regarded as "gas-metal" electrodes.

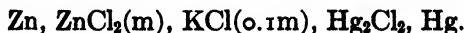
In discussing the results of the work of French and Kahlenberg, Blum⁴ disagrees with the statement that fundamental revision of the entire electrochemical series is required. He points out that the commonly accepted values of the potentials of the metals have been determined not in a solution of potassium chloride but in solutions of salts of the respective metals, each salt on solution yielding ions of the metal in question. He stresses the fact that the respective values in the electrochemical series are not so much an indication of the potential in a particular solution, as they are a measure of the tendency of the metal to go into solution in the form of ions. He further emphasizes the fact that to obtain a strictly reproducible potential it is absolutely necessary to exclude the possibility of more than a single reaction taking place at the electrode. This condition clearly does not obtain when the electrode is immersed in a solution of a salt which on dissociation does not yield ions of the metal whose potential is sought.

In a careful study of the nickel electrode, Haring and Vanden Bosche⁵ found that the potential of the metal was appreciably lowered by the presence of oxygen or air, and was correspondingly raised by the presence of hydrogen. In consequence of these facts they exercised special care to insure the exclusion of these gases in their final precise determinations of the electrode potential of nickel. The cell finally adopted by Haring and Vanden Bosche was the following



This will be seen to involve no liquid junction and to be completely reversible with respect to the nickel ion. The effects of oxygen and hydrogen on the potential of nickel were found to be directly opposite to those previously observed by French and Kahlenberg with nickel electrodes in normal potassium chloride.

In view of the foregoing work, it seemed of interest to study further the influence of air, oxygen, hydrogen and nitrogen on the potential of zinc when immersed in a solution of a zinc salt. To this end the following cell was chosen:



Materials

The zinc electrodes used were in the form of single crystals formed from metal of a high degree of purity.

⁴ Blum: *Trans. Am. Electrochem. Soc.*, **54**, 193 (1928).

⁵ Haring and Vanden Bosche: *J. Phys. Chem.*, **33**, 161 (1929).

The zinc chloride was prepared from Kahlbaum zinc by dissolving in pure hydrochloric acid. An excess of metal was added to the solution before concentrating, thereby minimizing acidity. When the solution had been evaporated to a syrupy consistency it was filtered through a column of pure zinc hydroxide into a liter flask where, after diluting with conductivity water, it was allowed to stand for a week or more. The molality of the solution was then determined by gravimetric estimation of the chloride ion as silver chloride, together with a measurement of its density by means of a pycnometer. The materials used in preparing the calomel electrode were of the high standard of purity specified for that purpose.

All gases used were obtained in pressure tanks and were found to be sufficiently pure after passing through appropriate saturators.

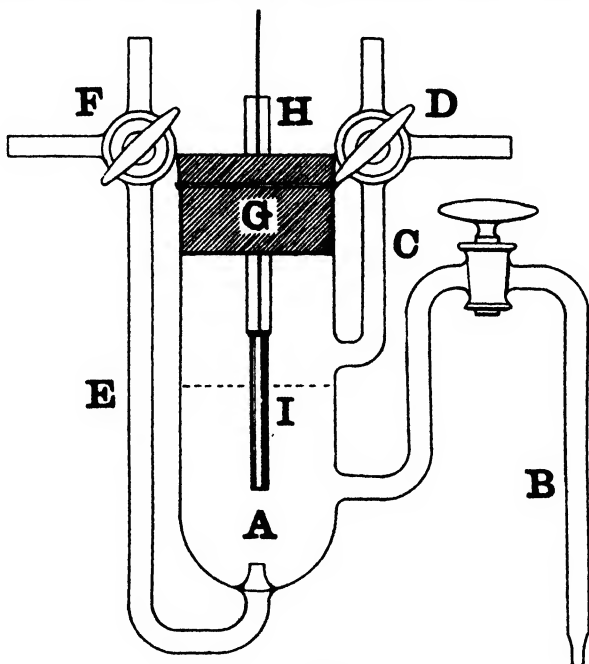


FIG. 1

Apparatus

A special electrode vessel, designed to facilitate the introduction and removal of both gases and electrolyte, was constructed of Pyrex, as shown in Fig. 1. Into the large tube A were sealed three side-tubes B, C and E. The tube B was furnished with a ground-glass stop-cock and served to connect the electrolyte, through a salt bridge of 0.1 m potassium chloride, to the calomel electrode. The tube E, fitted with a three-way stop-cock served to admit either gas or electrolyte into A as desired, while by means of the tube C and the three-way stop-cock D, connection with the air-pump could be established. The vessel was closed by means of a rubber stopper G carrying a glass tube H into which the single crystal electrode I was sealed. The under surface of

the stopper was coated with a film of paraffin to prevent absorption of gas by the rubber. To render the vessel air-tight a seal of Khotinsky cement was applied between the rim of A and the stopper. The electrode vessel, salt bridge and calomel electrode were immersed in a Freas' electrically heated and controlled thermostat the water of which was maintained at $25^{\circ} + 0.02^{\circ}\text{C}$.

All measurements of electromotive force were made by means of a Leeds and Northrup Type K potentiometer in conjunction with a suitable galvanometer and an Eppley standard cell.

Experimental Procedure

After the cell had been assembled it was placed in the thermostat and allowed to acquire the temperature of the bath. The stop-cock in the side-tube B and the stop-cock of the calomel electrode were then opened and the electromotive force of the combination was measured. Similar measurements were repeated at intervals of from fifteen to thirty minutes for a period of at least six hours. While the initial readings were found to fluctuate slightly, the readings after the first hour were quite constant and the average of the series served to establish what we shall term the "normal" potential. Having established the normal potential, a current of air was next aspirated through the electrolyte by connecting D with a jet pump and joining E with a saturator containing some of the same solution as in A. After having aspirated air through the electrolyte for twenty minutes, the stop-cocks D and F were closed and a new series of measurements was made at ten minute intervals over a period of three hours or more. The differences, ΔE , between the successive readings of the second series of measurements and the normal electromotive force were then plotted as ordinates against the time in minutes. Having determined the behavior of the electrode when immersed in the air-saturated electrolyte, the vessel A was emptied and, after thorough rinsing with fresh electrolyte, was refilled. The electrode was cleaned by dipping into a dilute solution of hydrochloric acid, washing in distilled water, drying with filter paper and then polishing with fine sand-paper. The clean electrode was replaced in A and the stopper G sealed air-tight with Khotinsky cement. The stop-cocks in B and E being closed, the vessel A and its contents were exhausted of air by means of a Hyvac pump connected at D. The exhaustion was continued until incipient ebullition was observed, when D was closed and the desired gas admitted through F. As in the case of air, measurements were made every ten minutes for the first three hours and then at less frequent intervals over an additional three or four hour period. The differences between the successive readings and the normal electromotive force were plotted against the corresponding times.

Experimental Results

It was soon found that no satisfactory duplication of results could be obtained when the experiments were repeated. While in most cases the influence of a given gas on the potential of a particular electrode in the same electrolyte was of the same order of magnitude, yet in the case of hydrogen especially,

the results obtained in different experiments were found to differ markedly and in some instances quite erratically. If the variations in potential produced by circumambient gas are due to adsorption, as we are inclined to believe to be the fact, it is hardly to be expected that successive runs would yield concordant results when we reflect that the conformation of the adsorbing surface of the electrode is materially altered by the abrasion of the sandpaper in the process of cleaning after each experiment. By taking the precaution to discontinue exhaustion with the commencement of ebullition of the electrolyte and also to bubble the gases through freshly charged saturators, it was found to be unnecessary to determine the concentration of the solution remaining in A after each experiment. A series of experiments was carried out with each gas in four different concentrations of electrolyte ranging from 0.049m to 0.9870m. With each of the gases it was found that the difference between the potential of the electrode and the normal potential determined at intervals over a period of several hours was practically independent of the concentration of the electrolyte. For this reason, and because of the difficulty of satisfactorily reproducing experimental data, it is only necessary to give a series of typical curves showing the manner in which the divergence of the electrode potential from the normal varies with the time for a single concentration of electrolyte. These curves for 0.1946m ZnCl_2 are shown in Fig. 2 while for comparison the corresponding curves of French and Kahlenberg for zinc in normal potassium chloride are reproduced in Fig. 3. Divergences from the normal electrode potential,—represented by a heavy horizontal line,—are plotted in millivolts $\times 10^{-1}$ against the corresponding intervals of time expressed in minutes. It will be observed that the scale of ordinates in Fig. 2 is ten-fold larger than that of Fig. 3. While in general the effects produced by oxygen, nitrogen, air and hydrogen on the potential of zinc in solutions of zinc chloride have been found to bear a close resemblance to those observed by French and Kahlenberg, it is important to note that the magnitude of the effect is by no means as large. The curves of Fig. 2 show that the initial value of the potential is increased by air, nitrogen and hydrogen, whereas it is decreased by oxygen. It is also apparent that the influence of each of the gases on the potential of the metal tends to diminish with time. In proof of the statement that duplication of results was well-nigh impossible, curves plotted from the data of two different runs with both oxygen and hydrogen are shown in Fig. 2. In the case of hydrogen, while the differences between corresponding values of ΔE on the two curves vary from 0.6 to 0.2 millivolts during the first hour, much greater differences are apparent after longer intervals of time. In the experiment designated as Hydrogen (a), ΔE had become practically zero at the end of seventy minutes. This suggested that the gas had probably diffused away from the electrode and, therefore, hydrogen was again passed through the electrode vessel for another ten minutes. The gas was then turned off and measurements resumed. As indicated by the solid circles in the diagram, the value of ΔE increased about 0.7 millivolt in consequence of this second treatment with gas and then gradually fell off with time. The behavior of the electrode in the experiment designated as

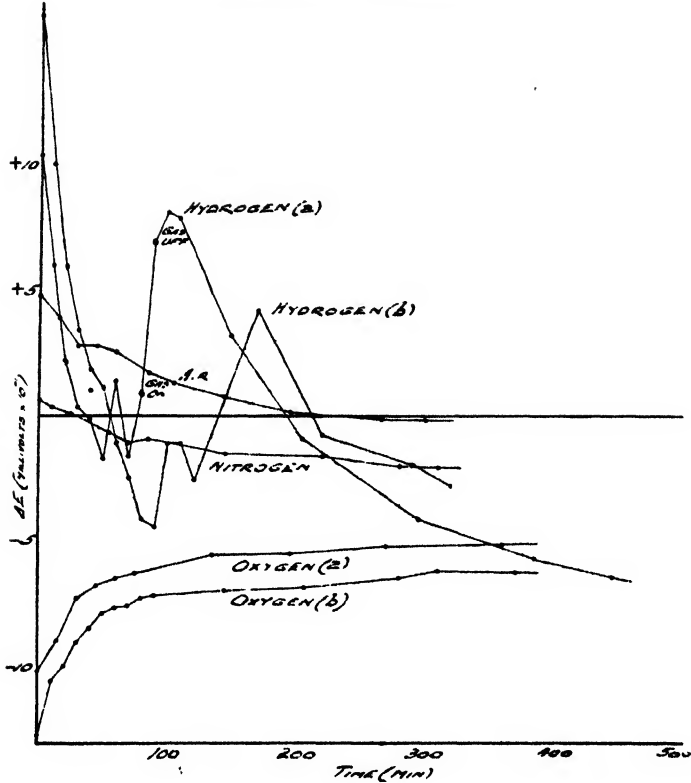


FIG. 2

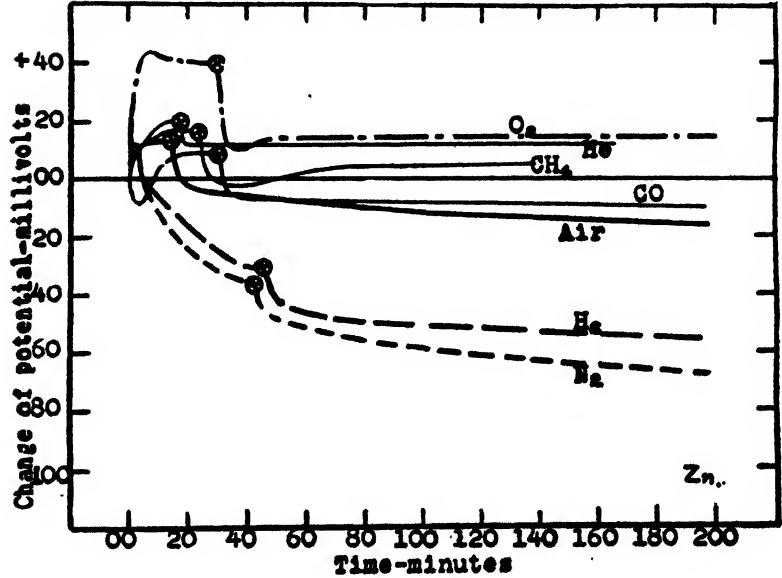


FIG. 3
 \otimes Gas shut off.

Hydrogen(b), however, differs from that of the preceding experiment in that a marked increase in ΔE occurred after the first seventy minutes without any additional treatment with gas. In all of the experiments with hydrogen sudden fluctuations of electrode potential similar to those shown in Fig. 2 were observed. If fact, one is almost led to suspect the existence of some periodic phenomenon similar to those recently described by Hedges and his coworkers.⁶ While the initial value of ΔE for oxygen is over 1 millivolt, it will be seen to have decreased to half-value within an interval of less than seven hours. In all of the experiments with oxygen, the curves were found to be quite free from fluctuations and their form was such as to suggest a logarithmic relation between the variables. When the logarithms of each of the two variables were plotted one against the other, the resulting graph was found to be linear, and hence the curves shown in Fig. 2 may be represented by an equation of the form

$$E = -bt^a,$$

where t denotes the time interval and where a and b are constants. On applying the equation to the experimental data from which the curves designated as Oxygen(a) and Oxygen(b) were plotted, the results given in Tables I and II were obtained.

TABLE I

t	$b = -15.14,$		$a = 0.1613$	Diff.
	E (calc.)	(E obs.)		
10	-10.44	-10.53		0.09
20	9.34	9.39		0.05
40	8.35	8.41		0.06
60	7.82	7.64		-0.18
80	7.46	7.18		-0.28
100	7.20	7.05		-0.15
120	6.99	6.86		-0.13
140	6.82	6.70		-0.12
160	6.68	6.58		-0.10
180	6.55	6.45		-0.10
200	6.44	6.38		-0.06
300	6.03	6.20		0.17

The close agreement between the calculated and observed values in the tables is such as to justify the conclusion that ΔE varies exponentially with the time when oxygen is present. This relation suggests that we are dealing

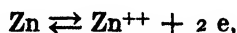
⁶ Hedges: J. Chem. Soc., 125, 604 (1924); 125, 1282 (1924); 127, 1013 (1925); 127, 2432 (1925); etc.

TABLE II

$b = -11.22, \quad a = 0.1357$			
t	E (calc.)	E (obs.)	Diff.
10	-8.21	8.30	0.09
20	7.47	7.50	0.03
40	6.80	6.83	0.03
60	6.44	6.45	0.01
80	6.18	6.20	0.02
100	6.01	5.95	-0.06
120	5.86	5.80	-0.06
140	5.74	5.70	-0.04
160	5.64	5.60	-0.04
180	5.55	5.56	+0.01
200	5.47	5.45	-0.02
300	5.17	5.20	+0.03

with a process of diffusion in which the initially adsorbed gas is gradually diffusing away from the electrode and thus permitting a gradual return toward the normal potential.

In reviewing the results of this investigation it would appear that when zinc is immersed in a solution of one of its salts, and hence can function as an electrode which is strictly reversible with respect to the ions of the metal, the reaction



takes precedence over all other reactions. Therefore, the influence of circumambient gas on the potential is much less pronounced than when the metal is immersed in a solution of some salt, such as potassium chloride, in which it cannot function reversibly.

The foregoing experiments afford confirmation of Dr. Blum's contention⁴ that the potential of a metal when immersed in a solution of a salt which does not yield ions of the metal on dissociation does not afford a measure of the potential of the reversible reaction upon which the commonly accepted value of its potential is based.

While our experiments with the zinc electrode have furnished abundant proof of the fact that the presence of gases exerts some influence on the potential of the metal, the magnitude of this effect is presumably lessened by the preponderating tendency of zinc to form zinc ions in the solution of zinc chloride.

Although the exclusion of all gases from the electrolyte is a safe precaution in precise measurements of electrode potentials, the foregoing experiments indicate that the practice of displacing air by means of a current of nitrogen should cause relatively little change in potential.

Summary

1. The effect of air, oxygen, nitrogen and hydrogen on the potential of zinc immersed in solutions of zinc chloride has been studied.
2. The initial value of the potential was found to be increased by air, nitrogen and hydrogen and to be decreased by oxygen.
3. The influence of each gas on the potential of the metal diminishes with time.
4. The divergence of the potential from its "normal" value produced by oxygen falls off exponentially with time.
5. The magnitude of the change in potential produced by the different gases has been found to be much less than the corresponding change produced by the same gases when the metal is immersed in a solution of potassium chloride.

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THE THERMAL DECOMPOSITION OF ZINC AND CADMIUM CARBONATES IN AN ATMOSPHERE OF WATER VAPOR

ALEXANDER LEHRMAN AND NATHAN SPEAR

The decomposition pressures of zinc and cadmium carbonates are difficult to measure due to the slowness of reaching equilibrium. A number of attempts have been made to measure the decomposition pressure of cadmium carbonate. W. Miethke¹ tried to measure it by a static method but found great difficulty in reaching a state of equilibrium, and furthermore could not duplicate his measurements. He points out that the presence of combined water in the carbonate is necessary for the system to approach equilibrium at a measurable rate. Tzentnershver and Andrusov² attempted the same measurement by static and dynamic methods and claim to have succeeded. The literature does not contain the report of any measurement on the decomposition pressure of zinc carbonate.

Even though Miethke states that the presence of combined water is necessary to enable the system cadmium carbonate-cadmium oxide-carbon dioxide to reach equilibrium, the authors decided to try the effect of having an atmosphere of water vapor present. The presence of one atmosphere of water vapor also makes possible a very simple method of determining the decomposition pressure of the carbonates.

No effort was made to obtain great accuracy. The work was carried out to test the effect of the presence of an atmosphere of water vapor and to see if the simplified method was possible. In view of this it is unnecessary to take into account the small effect of one atmosphere of inert gas (water vapor) on the decomposition pressure.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1. A is the bulb in which is placed the charge of carbonate and about 10 ml. of water. The bulb is made by sealing part of a pyrex test tube to a short piece of tubing. This is connected to the manometer tube B by heavy wall rubber tubing C. The left arm of the manometer tube is about 25 cm. long and the right one is about 80 cm. long. The manometer is immersed in an open beaker (4 liters capacity) of boiling water which is kept boiling by the hot plate F. The bulb is heated by the small electric heater G. This heater was made by setting the resistance coils of a resistance furnace in a box made of asbestos board and packed with 85% magnesia. The sides of the heater were asbestos board in which holes were cut just large enough to admit the bulb on one side and the thermocouple or thermometer on the other. When inserted the bulb and thermocouple or thermometer bulb were in the center of the air space in the heater, the end of the couple or thermometer bulb being in contact with the

¹ Dissertation, Berlin (1911).

² Z. physik. Chem., **123**, 111 (1926); **111**, 79 (1924); **115**, 273 (1925).

side of the bulb holding the carbonate. The temperature within the heating box was controlled by a hand-operated rheostat and switch. The temperatures above 300° were measured with a chromel-alumel thermocouple, and below this with a mercury thermometer. The thermometer was checked against the boiling point of water. Above 300° the temperature of the heater could be kept to within 5° of the desired temperature. Near the boiling point of water the temperature could be kept to within 1° of the desired temperature.

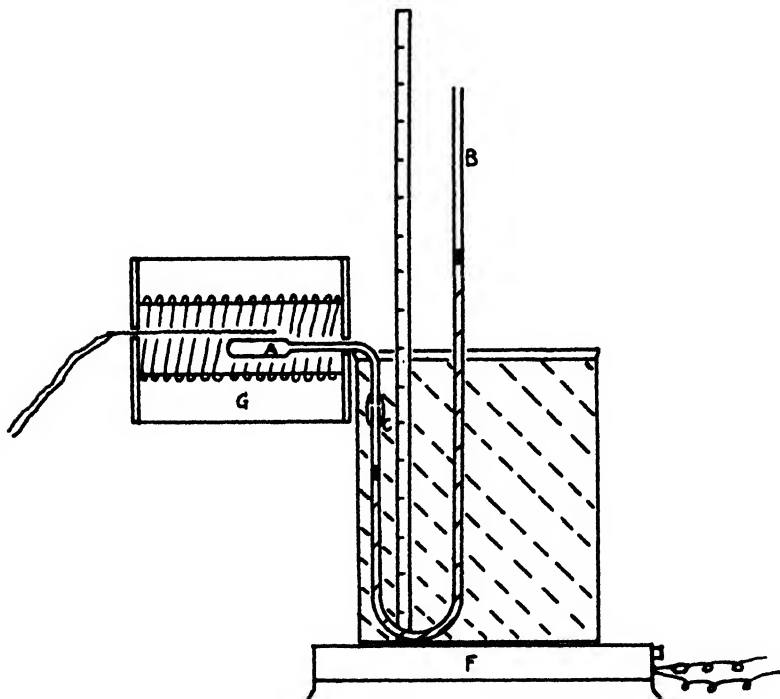


FIG. 1

The boiling water covered the short arm of the manometer tube and the tube connected to the bulb almost to the entrance to the heater. A meter stick was mounted in back of the manometer tube and the heights of mercury and water in the tubes were measured on this using a right-angle triangle to decrease errors of parallax.

Preparation of the Carbonates.—Cadmium carbonate was prepared by dissolving C. P. cadmium nitrate in water and precipitating the basic carbonate by addition of a solution of C.P. sodium carbonate. The precipitate was washed until the wash water gave no test for nitrates. It was then dissolved in concentrated ammonium hydroxide and carbon dioxide passed through until the solution was clear. The solution was then diluted with about fifty volumes of water and saturated with carbon dioxide. On standing a heavy crystalline precipitate settled out. This was washed with carbon-dioxide saturated water

and then with ethanol and air-dried. That the precipitate was crystalline could be seen when it was placed under a microscope. It was analyzed by heating a weighed sample in a combustion tube and drawing dry carbon dioxide-free air over it and then through weighing bottles containing soda lime and calcium chloride. It contained water, 3.3%; carbon dioxide 24.1%; and cadmium oxide 72.6%. This indicates a molar ratio of 1 H_2O : 3.0 CO_2 : 3.1 CdO .

The method did not work so well for the preparation of zinc carbonate. The precipitate formed on dilution of the solution of the basic zinc carbonate in ammonium hydroxide with carbon dioxide saturated water had 16.8% of water, 5.2% of carbon dioxide, and 78.0% of zinc oxide. This indicates a molar ratio of 1 CO_2 : 8.3 H_2O : 8.6 ZnO .

The exact nature of the precipitates is unknown. They may be compounds, mixtures, or solid solutions. Tests, however, showed that they were free from ammonia and from nitrates. The cadmium carbonate may be the normal cadmium carbonate. Miethke¹ showed that the normal cadmium carbonate is very insoluble. This may explain why it did not hydrolyze to the extent that the zinc salt did.

Method.—2 to 3 grams of the carbonate and 10 ml. of water were placed in the bulb and the bulb connected to the manometer. The manometer tube was put into the beaker of water as shown in Fig. 1 and the water in the beaker was brought to the boiling point and kept vigorously boiling. The heater was then brought up to the bulb and the temperature raised until the water in the bulb boiled. The steam formed passed into the manometer and swept out the air. Some of the water was condensed in the manometer tube and fell to the bottom of the U. The vapor produced after this condensed in the water and the absence of air was shown by the complete condensation of the bubbles in the water. Some of the carbonate was mechanically carried over into the manometer tube, but this could in no way affect the experiment. Warm mercury was then poured into the open end of the manometer and it sank through the water forming a continuous column with some liquid water on the top of both ends of the column. As the temperature of the bulb was raised more mercury was added. The liquid water on the top of the left-side column of mercury assured a pressure of one atmosphere of water vapor in the enclosed system, and which balanced atmospheric pressure on the right hand arm of the manometer. The difference in heights of the two columns was due to the carbon dioxide pressure of the carbonate.

The pressures were read by measuring the heights of the mercury and water columns on the meter stick. The pressures due to liquid water were converted to pressures in heights of mercury by dividing by 13.6. No corrections were made for the effect of temperature on the densities of water and of mercury as the errors introduced by this are less than the experimental errors.

At the close of each determination the heater was removed and the contents of the manometer rushed back into the bulb. The apparatus was then cleaned out and made ready for the next run.

Results.—Three efforts were made to measure the decomposition pressure of cadmium carbonate in this apparatus. Equilibrium, however, could not be attained and furthermore the pressures reached under the same conditions of time and temperature in the three runs were not concordant. We can say, however, that the decomposition pressure reaches one atmosphere at about 375° , which roughly checks previous work,¹ in which the pressure of water vapor was much less than one atmosphere. The presence of water vapor seems to exert no effect on the decomposition pressure of cadmium carbonate, neither in the time taken to reach equilibrium nor on the equilibrium pressure itself.

When the zinc carbonate was put into the apparatus, however, the pressure built up very rapidly to a high value at temperatures as low as 150° . In order to work with our apparatus we had to use temperatures between 100 and 120° and a mercury thermometer was substituted for the thermocouple. Furthermore, equilibrium was rapidly reached and the reaction reversed rapidly on cooling. The results of two determinations are listed in Tables I and II. Under these conditions the carbonate had an appreciable pressure just above 100° . Table I shows that at 110° a pressure of 30 cm is reached in 5 minutes. On heating to 120° a constant pressure of about 49 cm is reached in 10 minutes. Upon cooling to 110° the pressure rapidly falls to 30 cm and on heating again to 120° approximately 49 cm pressure is again obtained. The small deviations can be explained by deviations in temperature. Table II shows that at 105° a pressure of about 20 cm is reached in 20 minutes. The fluctuations in pressure are due to variations in the temperature which was controlled only to $\pm 1^{\circ}$. On heating to 110° a pressure of 28 cm is soon attained. This checks within our experimental error the value obtained in Table I. Upon cooling to 105° the reaction immediately reverses as shown by the pressure attaining its former value.

TABLE I

Temp. $^{\circ}\text{C}$	Pressure cm of Hg	Time minutes	Temp. $^{\circ}\text{C}$	Pressure cm of Hg	Time minutes
110	13	0	110	31.5	10
	30	5		30	15
	31.5	10		29.5	20
120	36	0	120	28.5	25
	48	5		30	30
	49	10		40.5	0
	49.5	15		44.5	5
	48.5	20		49.5	10
	49.5	25		46	15
110	36.5	0		46	25
	37.5	5			

TABLE II

Temp. °C	Pressure cm of Hg	Time minutes	Temp. °C	Pressure cm of Hg	Time minutes
105	14	0	110	27.5	10
	15	5		28	15
	13.5	10		28	20
	16	15	105	21	0
	21.5	20		19	5
	19.5	25		19	10
	19	30		20.5	15
	19	35		17	20
	21	40	110	25	0
	21	45		25	5
	21	50		25.5	10
	20	60		27	15
				27	20
110	27.5	0			
	27.5	5			

TABLE III

Temp. °C	Pressure cm of Hg	Time minutes	Temp. °C	Pressure cm of Hg	Time minutes
120	2	0	200	7	0
	3	30		10.5	5
	4	40		14	10
175				15	15
	5	0		16.5	20
	6.5	10		17.5	25
	7.5	20		19.5	35
	11	30	220	24	55
	13	40		25	65
	13.5	50			
	14	60		33	0
210				38	10
	23	0		52.5	20
	39.5	10		54	30
	47	20			
	50	30	200	53	0
105				53	10
	2	0		52.5	20
	1	10		52	30

For purposes of comparison a charge of zinc carbonate was put into a similar bulb and connected to a straight glass tube 90 cm long. This tube dipped into a bottle of mercury which carried a two-holed stopper. The arrangement served as a manometer. By tilting the apparatus the lower end of the tube was lifted clear of the mercury and the system evacuated through the second hole in the rubber stopper. A water aspirator was used. When the limit of evacuation was reached the apparatus was set upright and on discontinuing the action of the pump mercury rose in the tube. By comparing with a barometer the residual pressure was found to be 1.5 cm. On heating the bulb containing the carbonate, decomposition set in and the pressure of the carbon dioxide was measured by the depression of the mercury column. The results obtained are shown in Table III. It can be seen that the rate of thermal decomposition as well as the unattained decomposition pressure in the presence of only a slight pressure of water vapor is entirely different from that in an atmosphere of water vapor.

It may be that the reacting systems are different in the two cases. In the ordinary thermal decomposition the system may be represented by the components ZnO and CO_2 . In the decomposition in an atmosphere of water vapor the system may be ZnO , CO_2 and H_2O , or the action may be the hydrolysis of zinc carbonate as distinguished from its decomposition.

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HYDROLYSIS OF ACETONE IN ULTRA-VIOLET LIGHT

BY M. QURESHI AND N. A. TAHIR

That an aqueous solution of acetone is hydrolysed in ultra-violet light was first pointed out by Ciamician and Silber.¹ According to the observations of these authors, when the air is not completely excluded acetic and formic acids are formed. If, however, the air is completely excluded and solutions are exposed in sealed vessels, acetic acid and methane are the products of the reaction. Henri² determined the quantum efficiency (γ) of the reaction and found a value of 1300. The high value of γ found in these experiments was most probably due to the evaporation of acetone from the open quartz cell employed by Henri. Later, Brown and Watts³ using a closed cell of quartz with plane-parallel sides obtained values less than 0.2. The present investigation was undertaken with the object of determining (a) quantum efficiency of this reaction at different concentrations, (b) the influence of temperature on the quantum efficiency and the reaction-velocity, and (c) the influence of intensity on the rate of hydrolysis. The results, detailed below, have been obtained with heterogeneous ultra-violet light. Further experiments with mono-chromatic light and better methods of estimating the amount of acetic acid formed are in progress and will be reported afterwards. The discussion is postponed till the investigation is complete.

Procedure and Apparatus

A closed quartz cell with plane parallel walls was employed for exposing aqueous solutions of acetone. The amount of acetic acid formed was estimated by titrating against baryta, using phenolphthalein as indicator. A burette graduated to 0.02 cc. with a certificate of National Physical Laboratory was used for all titrations which were conducted in the light of a small electric lamp placed in a corner of the room away from the main apparatus. The usual method of preserving baryta solution in an atmosphere free from carbon dioxide and transferring it into the burette was adopted. The baryta solution was frequently standardised by means of oxalic acid. The apparatus employed was similar to the one used in a previous investigation on the photolysis of aqueous solutions of hydrogen peroxide, published in this Journal.⁴ The quartz cell containing the acetone solution found itself in a small bath having quartz windows on opposite sides into which water was pumped from a thermostat placed underneath on one side. The quartz bath had a small overflow opening near the top on one side through which water flowed back to

¹ Ber., 36, 1582 (1903).

² Compt. rend., 156, 1012 (1913).

³ J. Chem. Soc., 129, 1611 (1926).

⁴ J. Phys Chem., 36, 664-669 (1932).

the thermostat. The temperature of the thermostat was regulated in the usual way by means of an electric toluene regulator. In this way a continuous stream of water at a constant temperature was made to circulate through the small quartz bath. The source of light was a Quartz Mercury Lamp of the horizontal type manufactured by Hanovia Company. The lamp was placed inside a wooden box specially improvised for the purpose and lined inside with asbestos. A small electric fan placed inside behind the lamp served to ventilate the box. The ozonised air passed through an opening at the top of the box to a fume cupboard. The light of the lamp after passing through an opening in front of the box was converted into a parallel or converging beam by means of quartz lenses. A metallic reflector placed immediately behind the lamp served to increase the intensity of light. Lenses, diaphragm, quartz bath and thermopile were all mounted on an optical bench fixed permanently on a table just in front of the wooden box.

Quantum Efficiency at Different Concentrations

In these experiments acetone solutions of different concentrations were isolated in a quartz vessel with plain parallel walls, placed as described before in a small bath with quartz windows on opposite sides. The temperature of the bath was regulated at 30°C. For energy measurements a thermopile was placed immediately behind the bath and connected with a loop-galvanometer (Carl Zeiss) having an internal resistance of 6 to 10 ohms and sensitiveness of 3×10^{-7} amperes. The galvanometer was calibrated by means of a Heffner lamp both before and after the experiments. The deflections of the galvanometer were noted first with water and then with a solution of acetone in the quartz cell, the difference in the two readings corresponding to the amount of energy absorbed by the acetone solution. In calculating the number of light quanta the average wave length of the effective rays was taken as 313 m μ . After insulating acetone solutions for four hours the amount of acetic acid formed in each case was determined by carefully pipetting 5 c.cs. of the isolated solution into a small flask and titrating against baryta solution (0.012M.) The number of molecules of acetone hydrolysed per second was calculated from the amount of acetic acid formed. The ratio of this number to the number of light quanta absorbed per second gives the quantum efficiency of the reaction. The results of calculations are given below:

TABLE I

Molar concentration	Quantum efficiency γ	Molar concentration	Quantum efficiency γ
0.051	0.13	2.011	0.06
0.503	0.11	2.499	0.05
0.999	0.09	3.004	0.05
1.465	0.08	5.109	0.04

Effect of Temperature on the Quantum Efficiency

To find the effect of temperature on the quantum yield, the quantum efficiency (γ) of the reaction was determined, as previously described, at temperatures of 30°C. and 40°C. The concentration of the acetone solution was the same in each case. The following mean value of the temperature coefficient of the quantum yield was obtained from a number of determinations:

TABLE II

Temperature	Quantum efficiency	Temperature coefficient γ_{40}/γ_{30}
30°C.	0.12	1.41
40°C.	0.17	

Temperature Coefficient of the Reaction Velocity

To find the effect of temperature on the reaction velocity, acetone solutions of equal strength were insulated at temperatures of 30°C. and 40°C. in quartz vessels with plane parallel walls. The amount of acetic acid formed in each case was determined by titrating against the standard baryta solution (0.013 N.). Experimental conditions were the same in the two sets of experiments. The average results of a number of experiments are given below:

TABLE III

Concentration of the Solution = 0.044M

Temperature	Time of insolation	Amount of acetic acid in c.c.s. of baryta solution	Temperature coefficient k_{40}/k_{30}
30°C.	4 hours	0.085	1.52
40°C.	4 hours	0.130	

Effect of Intensity

The effect of intensity on the rate of hydrolysis of acetone was determined by two different methods. In the first set of experiments the intensity was varied by means of a rotating sector placed between the reaction vessel and the source of light. In the second set of experiments the aperture of the diaphragm was changed to vary the intensity. The amount of acetic acid formed in 4 hours with different sector openings and with different apertures of the diaphragm was determined by titrating against standard baryta solution. Temperature was kept constant at 30°C.

The results of these experiments are given in Tables IV and V.

TABLE IV

Method:		Rotating Sector	
		Velocity of Rotation = 500 revolutions per minute	
		Concentration = 1.439M.	
		Temperature = 30°C.	
Sector angle	Relative intensity	Amount of acetic acid formed in c.cs. of baryta solution	Rate of change <u>Intensity</u>
360°	4	0.12	0.03
180°	2	0.07	0.035
90°	1	0.03	0.03

TABLE V

Method:		Variation of diaphragm opening.	
		Concentration = 1.439M.	
		Temperature = 30°C.	
Relative intensity	Amount of acetic acid formed in c.cs. of baryta solution	Rate of change <u>Intensity</u>	
9	0.25	0.028	
4	0.14	0.035	
1	0.03	0.03	

Summary

1. The quantum efficiency of the hydrolysis of acetone in ultra-violet light was determined at different concentrations (0.05M-0.5M). Its value varies between 0.13 and 0.14.
2. The quantum efficiency was determined at two different temperatures viz. 30°C. and 40°C. The ratio of its values at these temperatures, i.e. the temperature coefficient of the quantum yield, is 1.41.
3. The temperature coefficient of the reaction velocity (k_{40}/k_{30}) is found equal to 1.52.
4. The influence of intensity on the rate of hydrolysis of acetone in ultra-violet light was determined by the methods of rotating sector and variation in the diaphragm opening. The results in both cases show that the rate of hydrolysis is directly proportional to the intensity.

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THE THEORY OF THE ADSORPTION OF GASES ON SOLIDS

BY R. S. BRADLEY

Adsorption is a very complicated process. It may be activated, or the energy of activation may be negligible, and the type of activation may change with the temperature. Lateral mobility of the adsorbed molecules, diffusion into the interior either through the lattice or more probably along crystallite boundaries, vibration perpendicular and parallel to the surface, collisions between adsorbed molecules and those striking the surface, or between adsorbed molecules on the surface, the rotation and dissociation of adsorbed molecules, may all have to be considered.¹ In this paper certain aspects of adsorption which have to do with the relation between the surface and bulk phases will be studied.

I. The Application of the 'Morse curve' to Adsorption

Frenkel² considered the potential energy of an adsorbed molecule to be of the form $-u_0 + \Delta u$, where Δu is given by the simple harmonic formula $2\pi^2/\tau_0^2 \cdot mz^2$: τ_0 is the period of oscillation perpendicular to the surface, m is the mass of the adsorbed molecule, and z is its distance from the equilibrium position. Instead of this parabolic curve it will certainly be closer to reality to use a potential energy curve of the form shown (Fig. 1). A good approximation to this type of curve was given by Morse³ in the form

$E(r) = u_0 e^{-2a(r-r_0)} - 2u_0 e^{-a(r-r_0)}$, where a is a constant connected with τ_0 by the relation $\frac{1}{\tau_0} = \frac{a}{2\pi} \left(\frac{2u_0}{m} \right)^{\frac{1}{2}}$, if the surface is regarded as a massive body at rest on which the adsorbed molecule oscillates. Hence $\Delta u = u_0 e^{-2as} - 2u_0 e^{-as} + u_0$, where $z = r - r_0$.

Frenkel calculated the thickness of the adsorption phase, δ , from the relation

$$\delta = \int_{-\infty}^{\infty} e^{-\Delta u/kT} dz = \tau_0 \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}}.$$

Then, applying $n/S = c_0 \delta e^{u_0/kT}$, $n = \nu\tau$,

$$\nu = S c_0 \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}}$$

(where n molecules are adsorbed on an area S , c_0 is the bulk concentration, and τ is the mean life of an adsorbed molecule: ν is the number of molecules striking an area S per second), we obtain

$$\tau = \tau_0 e^{u_0/kT}$$

On the basis of a 'Morse curve' this calculation becomes

$$\delta = \int_{-r_0}^{\infty} e^{-\Delta u/kT} dz = \frac{1}{a} \int_0^{\infty} \frac{e^{-c^2(u-1)^2}}{u} du,$$

where $u = e^{-as}$, e^{ar_0} is equal to ∞ , and $c^2 = u_0/kT$.

This integral may be split up into two parts, \int_1^{∞} and \int_0^1 . To evaluate

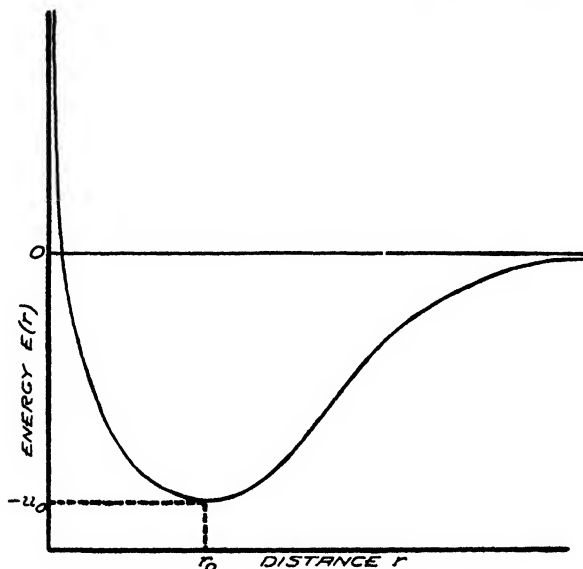


FIG. 1

the first part put $c(u-1) = w$. This gives

$$\frac{1}{a} \int_1^{\infty} \frac{e^{-c^2(c-1)^2}}{u} du = \frac{1}{a} \int_0^{\infty} \frac{e^{-w^2}}{w+c} dw$$

$$\begin{aligned} \text{Now } \int_0^{\infty} \frac{e^{-w^2}}{(w+c)^2} dw &= - \left[\frac{e^{-w^2}}{w+c} \right]_0^{\infty} - \int_0^{\infty} \frac{2w}{w+c} e^{-w^2} dw \\ &= \frac{1}{c} - 2 \int_0^{\infty} e^{-w^2} dw + 2c \int_0^{\infty} \frac{e^{-w^2}}{w+c} dw \end{aligned}$$

In practice c will be usually 4 or greater, corresponding to $u_0 = 10,000$ cals at room temperatures (even when u_0 is only 2500 cals c is 2). Hence we

may approximate to the value of $\int_0^{\infty} \frac{e^{-w^2}}{(w+c)^2} dw$ by putting $w = 0$, giving

$$\frac{\sqrt{\pi}}{2c^2} = \frac{1}{c} - \sqrt{\pi} + 2c \int_0^{\infty} \frac{e^{-w^2}}{w+c} dw$$

Hence the value of the first part is $1/a \cdot (\sqrt{\pi}/2c - 1/2c^2 + \dots)$ app. 2

$$\begin{aligned} \text{The second part is } & \frac{1}{a} \int_0^1 \frac{e^{-c^2(1-u)^2}}{u} du = \frac{1}{a} \int_{-c}^0 \frac{e^{-w^2}}{w+c} dw \\ & > \frac{1}{a} \int_{-c}^0 \frac{e^{-c^2}}{w+c} dw > \frac{1}{a} e^{-c^2} [\log(w+c)]_{-c}^0 = \infty. \end{aligned}$$

The method of Frenkel, therefore, does not give a finite result when applied to the more correct model. This difficulty may be removed by calculating the quantity adsorbed from the bulk gas, or the surface excess. If the number of molecules per cm^3 at the plane z is n_z , we may write

$$n_z = c_0 e^{u_0(-\Delta u/kT)} = c_0 \cdot e^{u_0/kT} \cdot e^{-\Delta u/kT} \quad 3$$

neglecting the size of the molecules. Hence the quantity adsorbed is given by

$$S c_0 e^{u_0/kT} \int_{-r_0}^{\infty} (e^{-u\Delta/kT} - 1) dz = \frac{S c_0}{a} e^{u_0/kT} \int_{-c}^{\infty} \left(\frac{e^{-w^2} - e^{-c^2}}{w+c} \right) dw$$

The last integral is now finite when $w = -c$, for on putting $w = -c + \epsilon$,

$$\frac{e^{-w^2} - e^{-c^2}}{w+c} = e^{-c^2} \left(\frac{e^{-\epsilon^2+2\epsilon c} - 1}{\epsilon} \right) = \frac{e^{-c^2}}{\epsilon} (\epsilon^2 + 2c\epsilon \dots) = 2ce^{-c^2} \text{ when } \epsilon \rightarrow 0.$$

As before $\int_{-c}^{\infty} \frac{e^{-w^2} - e^{-c^2}}{w+c} dw$ may be split up into two parts.

a) $\int_0^{\infty} \frac{e^{-w^2}}{w+c} dw$ has been calculated. $\int_0^{\infty} \frac{e^{-c^2}}{w+c} dw = \int_{-r_0}^0 e^{-c^2} dz = e^{-c^2} r_0$, and is negligible.

b) $\int_{-c}^0 \frac{e^{-w^2} - e^{-c^2}}{w+c} dw = I$. When c is of the order 4 it will be suf-

ficiently accurate to take $I = \int_{-c/2}^0 \frac{e^{-w^2}}{w+c} dw$, since the contribution of the term e^{-c^2} is small in this range, and since the value of the integral in the range $-c/2$ to $-c$ is small compared with the portion in the range $-c/2$ to 0.

$$\text{Now } \int_0^{-c/2} \frac{e^{-w^2}}{(w+c)^2} dw = \left[-\frac{e^{-w^2}}{w+c} \right]_0^{-c/2} - 2 \int_0^{-c/2} e^{-w^2} dw + 2c \int_0^{-c/2} \frac{e^{-w^2}}{w+c} dw.$$

Hence, as before, $I = \sqrt{\pi}/2c - 1/2c^2$. The quantity adsorbed is therefore

$$n = \frac{S c_0}{a} \cdot e^{u_0/kT} \left(\frac{\sqrt{\pi}}{c} - \frac{1}{c^2} \right)$$

On inserting the value of a , and on putting $n/\tau = \nu$ we get

$$\tau = \tau_0 \left(1 - \sqrt{\frac{kT}{\pi u_0}} \right) e^{u_0/kT}$$

as the modified Frenkel relationship. It will be noticed that the correction is small, but that Frenkel's definition of δ should run $\delta = \int_{-\infty}^{\infty} (e^{-\Delta u/kT} - 1) dz$.

This definition will not give a finite value for δ when the potential energy curve is parabolic, and only by combination of inexact definitions of δ and of the potential energy curve can a finite result be obtained by Frenkel's method.

II. The Unimolecular Film

In the above treatment, using the Morse curve, τ_0 appears merely as a constant in the potential energy curve, and no reference is made to the actual oscillations of the adsorbed molecules. Equation 3 gives a gradually increasing concentration up to the minimum in the potential energy curve. In actual practice the bulk of the adsorbed film will probably be confined to a unimolecular layer, not necessarily closely packed, and secondary adsorption, if it occurs (as for example with water), will be weaker. It is also desirable for simplicity to regard the adsorption as unimolecular, for a molecule in the second layer will not have the same potential energy curve as one in the first.

At first sight there seems little connection between this point of view and the one in which the concentration is supposed to vary continuously up to the surface. But any given molecule of the unimolecular film will be oscillating, and will spend most of its time at the extreme positions of its oscillations. As an approximation suppose it spends all its time there. Then we again get a "static" spatial distribution. If there are n_0 mols. per cm^3 at the equilibrium position the number at the plane z is $n_0 e^{-\Delta u/kT}$ and at the plane ∞ $n_0 e^{-u_0/kT} = c_0$, where c_0 is the bulk concentration. Hence as before

$$n = S \int_{-r_0}^{\infty} (n_0 e^{-\Delta u/kT} - c_0) dz = S c_0 \int_{-r_0}^{\infty} (e^{-Ez/kT} - 1) dz$$

Owing therefore to oscillation the unimolecular film gives a volume distribution as before. This spatial unimolecular layer is really what is considered in section I, since a molecule in the second layer as ordinarily defined will not have the same oscillation constants as one in the first layer.

III. Correction for the Finite Size of the Adsorbed Molecules

When part of the available space is excluded because of the finite size of the molecules equation 3 can no longer be applied. This correction is important, because the concentration near the surface is high.

Let v_0 be the volume of a molecule. Then equation 3 could be replaced by

$$\frac{n_s}{1 - n_s v_0} = \frac{c_0 e^{-E_s/kT}}{1 - c_0 v_0} = c_0 e^{-E_s/kT}, \text{ since } c_0 v_0 \ll 1.$$

This equation gives $n_s = 1/v_o$ when E_s is very large, as it should, for then close packing will occur.

Hence

$$\begin{aligned} n &= S \int_{-r_o}^{\infty} (n_s - c_o) dz \\ &= S \int_{-r_o}^{\infty} \left(\frac{c_o e^{-E_s/kT}}{1 + c_o v_o e^{-E_s/kT}} - c_o \right) dz \end{aligned}$$

This equation cannot be integrated as it stands, although a graphical evaluation is of course possible when E_s is known. An approximation can however be obtained as follows.

$$\begin{aligned} n &= S c_o e^{u_o/kT} \int_{-r_o}^{\infty} \left(\frac{e^{-\Delta u/kT}}{1 + c_o v_o e^{-E_s/kT}} - e^{-u_o/kT} \right) dz \\ &= S c_o e^{u_o/kT} \int_{-r_o}^{\infty} (1 - n_s v_o) (e^{-\Delta u/kT} - e^{-u_o/kT}) dz \end{aligned}$$

Now replace $1 - n_s v_o$ by its mean value between the limits $-d/2$ and $d/2$, where d is the molecular diameter. The major portion of the integral will fall in these limits

$$\therefore \int_{-d/2}^{d/2} n_s dz = n/S \text{ app.}$$

\therefore mean value of $n_s = n/dS$

$$\text{and mean value of } 1 - n_s v_o = 1 - \frac{nv_o}{Sd} = \frac{S - n\sigma_o}{S}$$

where σ_o is the area on the surface appropriated by one molecule and into which another cannot enter.

$$\begin{aligned} \text{Hence } \frac{n}{S - n\sigma_o} &= c_o e^{u_o/kT} \int_{-r_o}^{\infty} (e^{-\Delta u/kT} - e^{-u_o/kT}) dz \\ &= \frac{c_o}{a} e^{u_o/kT} \left(\frac{\sqrt{\pi}}{c} - \frac{1}{c^2} \right) \\ &= \frac{c_o}{a} e^{u_o/kT} \frac{\sqrt{\pi}}{c} \left(1 - \sqrt{\frac{Tk}{\pi u_o}} \right) \end{aligned}$$

This is, in fact, the form of Langmuir's isotherm, and we see that this form is determined by the allowance for the finite volume of the molecules.

IV. The Mean Life of Adsorbed Molecules and the Adsorption Isotherm

It follows therefore that Frenkel's deduction of the mean life of an adsorbed molecule must be revised, for in that deduction proportionality was taken between quantity adsorbed and the pressure. Before this is done, how-

ever, another correction to Frenkel's calculation must also be applied, namely, an allowance for the reflexion coefficient.

Let a fraction e be reflected from the surface. Then

$$n/\tau = (1 - e) \nu$$

e is dependent on the surface concentration. For suppose a molecule from the gas on hitting an adsorbed molecule is either reflected (fraction x), or is reflected with the adsorbed molecule, which has been activated for desorption by collision (fraction y): finally a fraction z may be adsorbed by displacing to the side the molecule on the surface with which the gas molecule collides. Then $x + y + z = 1$. On the other hand suppose that a molecule on hitting a free space is adsorbed with probability β .⁴

$$\begin{aligned} \text{Then } e &= n\sigma_0/S \cdot (x + 2y - z) + (1 - \beta) (1 - n\sigma_0/S) \\ &= n\sigma_0/S \cdot (1 + y - 2z) + (1 - \beta) (1 - n\sigma_0/S) \end{aligned}$$

$$\text{Hence } (1 - e) = \beta - n\sigma_0/S \cdot (y + \beta - 2z).$$

When, therefore, the surface is closely crowded, $1 - e = 2z - y$. Normally, however, $y - 2z$ may be neglected compared with β , and hence

$$(1 - e) = \beta (1 - n\sigma_0/S) \text{ and } n/\tau = \beta\nu/S \cdot (S - n\sigma_0) \quad 4$$

On combining this result with the equations

$$\begin{aligned} \frac{n}{S - n\sigma_0} &= c_0 \frac{1}{a} e^{u_0/kT} \frac{\sqrt{\pi}}{c} \text{ app.} \\ \frac{1}{\tau_0} &= \frac{a}{2\pi} \left(\frac{2u_0}{m} \right)^{\frac{1}{2}} \\ \nu &= S c_0 \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} \end{aligned}$$

$$\text{we get } \beta\tau = \tau_0 e^{u_0/kT} \quad 5$$

$$\text{Now from 4} \quad n = \frac{\beta\nu\tau S}{S + \sigma_0\beta\nu\tau} \text{ (Langmuir's isotherm)}$$

$$\text{Hence} \quad \frac{n}{S} = \frac{\tau_0 e^{u_0/kT} p / (2\pi mkT)^{\frac{1}{2}}}{1 + \tau_0 \sigma_0 e^{u_0/kT} p / (2\pi mkT)^{\frac{1}{2}}}$$

where p is the bulk pressure. This is the equation Frenkel deduced, although he obtained it by neglecting β , and by inserting in Langmuir's equation (in which n is not proportional to the pressure) the result $\tau = \tau_0 e^{u_0/kT}$ deduced on the assumption of proportionality between n and the pressure.

$$\text{On writing the isotherm in the usual form } \frac{n}{S} = \frac{c_1 c_2 p}{1 + c_2 p}$$

$$\text{we have} \quad c_1 c_2 = \frac{\tau_0 e^{u_0/kT}}{(2\pi mkT)^{\frac{1}{2}}} \quad 6$$

$$c_1 = 1/\sigma_0 \quad 7$$

The form 6 was deduced by Bradley⁵ from general thermodynamic reasoning, neglecting the small effect of the power of T in the temperature coefficient, and shown to agree with experiment. Little can be said on the variation of c_1 with temperature given by equation 7.

V. The Formation of Agglomerates on the Surface

Frenkel explained the existence of a critical temperature for the condensation of atomic beams by the formation of pairs of combined atoms on the surface. When an allowance is made for the reflection coefficient the deduction for the critical stream density must be modified. For then

$$dn/dt = \nu (1 - e) = w_1 n_1 - w_2 n_2$$

where there are n_1 and n_2 single and double molecules on the surface of mean lives $1/w_1$ and $1/w_2$. Hence at equilibrium $\nu\beta(1 - n\sigma^\circ/S) - w_1 n_1 - w_2 n_2 = 0$

$$\nu\beta(1 - n\sigma_0/S) - w_1(n - n^2\sigma/S) - w_2 n^2\sigma/S = 0, \text{ where } \sigma = \sigma_0 e^{E_0/kT},$$

and E_0 is the dissociation energy of the doublet ($\sigma > \sigma_0$).

Hence $\frac{n^2\sigma}{S} (w_1 - w_2) - n \left(w_1 + \frac{\nu\beta\sigma_0}{S} \right) + \nu\beta = 0$, and n is real only if

$$\left(w_1 + \frac{\nu\beta\sigma_0}{S} \right)^2 > 4 \frac{\beta\sigma}{S} (w_1 - w_2)\nu > 4\nu\beta\beta' \text{ where } \beta' = \frac{\sigma}{S} (w_1 - w_2)$$

The critical value of ν is given by $\frac{\nu^2\beta^2\sigma^2}{S^2} + \nu \left(\frac{2w_1\beta\sigma_0}{S} - 4\beta\beta' \right) + w_1^2 = 0$,

$$\text{or } \nu = \left[4\beta\beta' - 2\frac{w_1\beta\sigma_0}{S} \pm 4\sqrt{\beta^2\beta'^2 - \frac{w_1\beta^2\beta'\sigma_0}{S}} \right] \frac{S^2}{2\beta^2\sigma^2}$$

in place of Frenkel's relation $\nu = \frac{w_1^2}{4(w_1 - w_2)} \frac{S}{\sigma}$

The term under the root is $\beta^2\beta'^2 \left(1 - \frac{w_1\sigma_0}{\beta'S} \right)$, and if $w_1 - w_2$ is of the same

order as w_1 , $\frac{w_1\sigma_0}{\beta'S}$ is small.

$$\text{Hence } \frac{2\beta^2\sigma^2\nu}{S^2} = 4\beta\beta' - 2\frac{w_1\beta\sigma_0}{S} \pm \left(4\beta\beta' - 2\frac{\beta w_1\sigma_0}{S} - \frac{w_1^2\beta\sigma_0^2}{2\beta'S^2} \dots \right)$$

$$\text{and } \nu = 4\sigma(w_1 - w_2) \frac{S}{\sigma_0^2\beta} \text{ or } \frac{w_1^2 S}{4\beta\sigma(w_1 - w_2)}$$

When, therefore $\nu > \frac{w_1^2 S}{4\beta\sigma(w_1 - w_2)}$ and $< 4\frac{\sigma}{\sigma_0^2\beta} (w_1 - w_2)S$ the value

of $\frac{\nu^2\beta^2\sigma^2}{S^2} + \nu \left(\frac{2w_1\beta\sigma_0}{S} - 4\beta\beta' \right) + w_1^2$ is negative, and n is not real. No equilibrium exists between these limits. There are two critical points instead of one.

This result is still obtained if the theory is elaborated in terms of potential energy curves between pairs of molecules on the surface. Let the energy

curve between two molecules be $E(r)$, where r is measured along the surface. Select one molecule. Then the chance that the centre of a second molecule is between r and $r + dr$ of the centre of the first is $\frac{2\pi r \cdot dr}{S}$. This assumes that all parts of the surface are equally accessible to the second molecule, and that the first molecule is not on the edge of S .

Since there are n molecules on S the chance that any one of these has its centre between r and $r + dr$ of that of the selected molecule is $\frac{2\pi r \cdot dr}{S} \frac{1}{2}n(n-1)$, since each pair will be counted twice. Owing to the intermolecular force this will become $\frac{\pi r \cdot dr}{S} n(n-1) e^{-E(r)/kT}$.

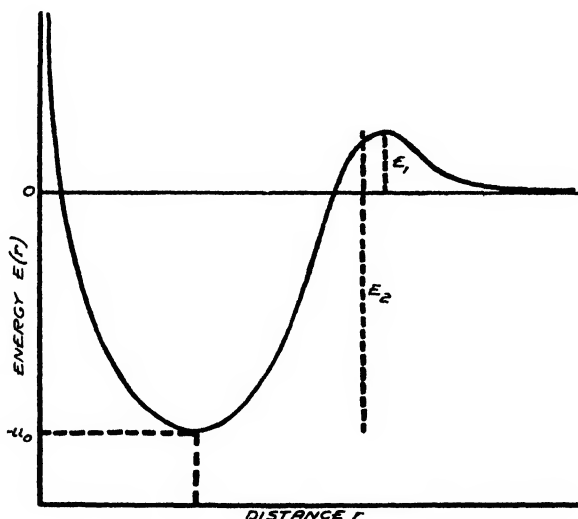


FIG. 2

Theoretically the influence of one molecule on another extends to great distances. Actually, however, at distances greater than some value d_1 the effect of one molecule on another will be negligible. Those pairs with centres less than d_1 apart may be regarded as a double molecule.

$$\text{Hence } \frac{dn}{dt} = \nu(1 - e) - w_1 \left(n - \int_0^{d_1} \frac{\pi n^2}{S} e^{-E(r)/kT} \cdot r \cdot dr \right) - \int_0^{d_1} \frac{n^2 \pi}{S} e^{-E(r)/kT} r w_r dr$$

where w_r is the value of $1/\tau_r$, and τ_r is the mean life of a molecule in a pair with centres a distance r apart. The last equation is of the form

$$\frac{dn}{dt} = \beta \nu \left(1 - \frac{n\sigma_0}{S} \right) - w_1 [n - n^2 \Phi(d_1)] - n^2 \Omega(d_1),$$

of the same type as before.

VII. Activated Adsorption

It may happen that β corresponds to an activated adsorption,⁶ only a fraction $e^{-E_1/kT}$ of the impinging molecules entering the adsorption phase. Then the relation $\beta\tau = \tau_0 e^{u_0/kT}$ becomes $\tau = \tau_0 e^{E_1/kT}$, (instead of $\tau = \tau_0 e^{u_0/kT}$), where E_1 is the activation energy required for desorption. This gives a form for the rate of desorption which is independent of the reverse reaction. E_1 can be accounted for by a potential energy curve of the type shown (Fig. 2). The calculation of δ will not be affected by the small rising of the curve above the zero axis, as the contribution to the integral of this portion is small. However the rate of desorption will be affected. The adsorbed molecules will have various amplitudes, corresponding to various energy levels, and strictly they will be anharmonic oscillators, the frequency varying with the amplitude. For simplicity suppose that they all have the same frequency $1/\tau_0$. Any particular molecule will leave the surface when its energy, kinetic and potential, exceeds the energy at the lowest point of the potential energy curve by E_1 , taking this lowest point as the zero reference point for the energy. A molecule has a chance to evaporate $1/\tau_0$ times per second, and if all the molecules were activated the rate of evaporation would be n/τ_0 per area S. Only a fraction $e^{-E_1/kT}$ is activated, however, and supposing that the supply of active molecules can be maintained the rate of evaporation will be $n/\tau_0 e^{-E_1/kT} = n/\tau$, giving the required relation. It is interesting to notice that Alty's⁷ results on the evaporation of water can be interpreted by writing his absorption coefficients in the form $e^{-E_1/kT}$ where E_1 is about 2600 cal.

If desorption resembles the dissociation of a molecule in this way there is the interesting possibility that the activation may be effected by means of a light quantum.

My thanks are due to Mr. Gilham for mathematical advice.

References

- ¹ See Trans. Faraday Soc., **28**, Parts 3 and 4 (1932).
- ² Frenkel: Z. Physik, **26**, 117 (1924).
- ³ Morse: Phys. Rev., (2) **34**, 57 (1929).
- ⁴ See also Clausius: Ann. Physik, [5] **7**, 489, 522 (1930).
- ⁵ Bradley: Phil. Mag., **11**, 690 (1931). The equation of page 695 should run $1/c_1 = .05073 - 16.26/T + 3.10^4/T^2$, giving a constant value to c_1 at high temperatures as stated.
- ⁶ Taylor: Trans. Faraday Soc., 1932, Parts 3 and 4.
- ⁷ Alty: Proc. Roy. Soc., **131A**, 554 (1931).

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NEW BOOKS

An Introduction to the Principles of Physical Chemistry. By O. Maass and E. W. R. Steacie. 24 × 16 cm; pp. vii + 277. New York and London: John Wiley and Sons, Chapman and Hall, 1931. Price: \$2.75. "This book is intended to be used as a first course in physical chemistry for students who have had elementary courses in chemistry, physics, and mathematics. A course of about 50 lectures has been given at McGill University for the past 12 years in this form to a class composed of those intending to make chemistry their profession, chemical engineers, and students intending to enter medicine and the biological sciences. These students have either not had calculus, or are taking courses in it concurrently with physical chemistry. In the case of students intending to specialize in chemistry it has been found advisable to bring in an elementary course such as this at the earliest possible stage in their training. This makes possible a better appreciation of more advanced and detailed courses in physical chemistry, since the student thus has several years in which to assimilate the fundamental ideas," p. v.

The chapters are entitled: introduction; the structure of matter; the gaseous state of aggregation; the transition from the gaseous to the liquid state; the liquid state of aggregation; the solid state of aggregation; energy and the structure of matter; mixtures, solutions, and compounds; solutions; the theory of solutions; chemical equilibria; the velocity of chemical reactions; electrolytic dissociation; applications of the ionic hypothesis; thermochemistry.

As emphasized in the preface the authors believe in giving an introductory and a more advanced course in physical chemistry. One justification for this is given on p. 2. "Today specialization in a fairly narrow field is necessary. Although this is true, it is nevertheless essential that phenomena which apparently differ widely should be correlated as much as possible. Hence, in order to pursue one branch of science successfully, it is necessary to have a working knowledge of all related subjects."

Another justification is given on p. 10. "Among the prerequisites for a comprehensive study of physical chemistry mathematics takes an important place. It does so from two rather different points of view. Of these, the ability to utilize mathematical manipulations in specific problems in physical chemistry is perhaps of less importance than the training in exact thinking and in certain logical systems of reasoning. Except in a few minor divisions of physical chemistry the mathematical technique required is of the simplest kind, involving only the elementary principles of calculus and analytical geometry. For an elementary introduction to the subject, such as this book, even these are not required to any great extent."

The reviewer believes that the authors are right in their point of view and that chemists should be given a general knowledge of physical chemistry with as little mathematics as possible. After that the mathematically inclined can follow their natural bent. On p. 172 the authors say that "solution is thus completely analogous to evaporation." They are thinking unconsciously in terms of mathematics. The reviewer would like to see the further statement that "solution is thus completely analogous to melting. A solution is a mixture of liquids. The gas laws are applicable to some extent to the components."

"In the case of water, the data indicate that the molecules in the liquid state are partly $(\text{H}_2\text{O})_2$ and partly $(\text{H}_2\text{O})_3$. These are referred to as dihydrol and trihydrol, respectively. In the case of the latter, for example, there are 9 atoms in the molecule. These move about as a separate and distinct unit. None of them can be displaced without the displacement of the remainder in such a way as to preserve their relative positions. Liquid water is thus a mixture of different molecules, and all we can do is to assign to it an average molecular weight," p. 106.

"The second law [of thermodynamics] is based on experimentally observable systems, in which the average velocity of a large number of molecules is under consideration. The second law is only a statistical truth, which holds when the number of molecules concerned is large. That Maxwell's suggested mechanism is actually observable experimentally will be made evident later in connection with the Brownian movement of colloidal particles," p. 119.

On the assumption that the hydrogen ion is not hydrated, the authors give the following values, p. 221, for some other ions: K, 20; Ag, 35; Cu, 55; Na, 70; Li, 150; OH, 10; Cl, 20; NO₃, 25. It is undoubtedly perfectly safe to believe that these values are not right.

Wilder D. Bancroft

Smoke: A Study of Aerial Disperse Systems. By R. Whytlaw-Gray and H. S. Patterson. Pp. viii + 192. London: Edward Arnold and Company, 1932. Price: 14 shillings. The study of those disperse systems in which a liquid or solid substance is dispersed in a very finely divided condition in a gas or vapour is of peculiar interest to the physical chemist. It leads to such interesting problems as the precise mechanism of smoke formation by the condensation—under many guises—of a diluted vapour, the manner of growth of the freshly formed particles, the extent to which the subsequent behaviour of the particles is affected by the adsorption of gas molecules or ions, the possibility of the smoke particles exerting a catalytic action upon a reaction between two or more constituents of the dispersion medium, and the mechanism by which the smoke particles themselves may react directly with some constituent of the gas mixture.

To the student of colloid chemistry, considered from its simplest aspect—the physical and chemical activity of finely divided matter—smokes provide a comparatively simple system for investigation.

To obtain the data necessary for a quantitative study of the formation and behaviour of these gaseous disperse systems, it has been found necessary to develop a special experimental technique. This has been done with remarkable skill and ingenuity by the authors of the book under review.

The book opens with an introductory discussion of the nature and structure of smoke and an account of the earliest systematic attempts, made some fourteen years ago, to determine the mass concentration of smokes, the size of the particles and the number of particles per unit volume, and the way in which these characteristic quantities change with time. These early methods were subject to error, owing to the difficulty of illuminating sufficiently all the particles in the field of the ultramicroscope.

The improved methods that have been developed by the authors are described, and a full account is given of the ingenious method of H. L. Green, in which the ultramicroscopic visibility of the very fine particles is increased by condensing water vapour upon them, while the errors due to faulty observation are eliminated by actually photographing the particles within the field of view.

The authors show how the experimental methods can be applied to the systematic study of smoke coagulation, and a theory of coagulation, based upon that of Smoluchowsky for homogeneous sols, is developed and shown to be adequately justified by the experimental data.

The authors adopt two methods of smoke formation: In the first, they dilute and chill a small quantity of the hot vapour of a high boiling-point substance, such as stearic acid or resin, with a blast of cold air. In the second, they blow a gentle stream of air across an arc struck between poles of metals such as zinc, cadmium or magnesium. They point out that von Weimarn's theory cannot be applied satisfactorily to the study of smokes formed in this way since, during the formation of the smoke, the temperature is continually changing, and with it the degree of supersaturation. Possibly, however, the theory might be applied usefully to the study of smokes formed by chemical interaction between two gases such as ammonia and hydrogen chloride. Using such a method, the initial concentrations and the temperatures and pressures of the two gases could be varied widely, and the effect of other

gases and vapours upon the nature of the particles formed could be investigated. By this means, possibly, the early stages of particle formation could be controlled more completely and the effect of individual factors observed more accurately. It would be interesting to know why the authors decided not to use this method of smoke formation.

One of the most interesting chapters in the book is that which deals with the growth and structure of smoke particles of different substances. Apparently, the ultimate form of a smoke particle, whether crystalline, spherical or chain-like, depends primarily upon the temperature at which the smoke is formed, the rate of crystallisation of the material and the way in which the primary particles are electrified.

A very full account is given of the technique employed for the determination of the weight concentration of the smoke, of the size and density of the individual particles and their size distribution in the smoke. The scattering of light by smokes and the curious phenomenon of photophoresis are well described. Other important chapters deal with the electrification of smoke particles and with the evaporation of small droplets. The book concludes with a stimulating and suggestive chapter, indicating some of the lines along which further research might profitably be carried out.

The authors have carried out a fine piece of pioneer investigation with conspicuous success. The book is valuable for the clear and full description which it contains of their experimental methods and of the way in which they can be applied to the study of the formation and the behaviour of smokes. The book can be recommended heartily to all who are interested in smokes, either from the purely physico-chemical standpoint or from the standpoint of the chemical engineer—that applied physical chemist—who so often is called upon to control smoke-producing reactions, to clarify turbid gases and vapours or to manufacture finely divided pigments and catalytic substances from gases. The book is written in a lucid and interesting manner; it is well illustrated, and can be thoroughly recommended as a stimulating introduction to a new and fascinating field of investigation.

W. E. Gibbs

Von Davy und Döbereiner bis Deacon. By A. Mittasch and E. Theis. 23 × 16 cm; pp. 278. Berlin: Verlag Chemie, 1932. Price: 18.50 marks. The potentialities in the applications of surface catalysis to industrial problems of the most varied character were probably first realised to the greatest extent in those varied German undertakings now represented by the I. G. It is a graceful appreciation of this fact that has prompted Dr. A. Mittasch (of the research laboratory at Oppau) and Dr. Theis to celebrate the close of the first fifty years of scientific attainments in this field by presenting us with this volume. The historical development of the subject during these early years is entwined around the names of a few distinguished men and these have been used to focus our attention both on the advances and on the difficulties contracting the pioneers.

During the last fifty years the number of papers which have appeared in the scientific press dealing with the subject of catalytic oxidation must run into the hundreds if not thousands. In all probability few, if any, of the writers of these papers have troubled to read, far less re-read, the work of Davy and Döbereiner and the subsequent work of Faraday and Schönbein. In the United States, Professor Bancroft has called attention again and again both to the importance of and interest to be found in such reading and our thanks are due to these authors in adopting this method of sketching the historical development of such an interesting subject.

Amongst other names included in the text are to be found those of Thénard, Berzelius, Liebig and Mitscherlich, whilst the early technical development of the subject is presented to us in the form of an account of the origins of the sulphuric acid contact process, and synthesis and oxidation of ammonia and the Deacon process.

The book is very readable, well printed and contains the portraits of sixteen distinguished men.

Eric K. Rideal

Lichtelektrische Zellen und ihre Anwendungen. By H. Simon and R. Suhrmann. 22 × 15 cm: pp. viii + 373; Berlin: Julius Springer, 1932. Price 33 marks, bound 34.20 marks. I am really the last person who ought to review this book, for I am part author of the only English (as distinct from American) book likely to come into competition with it. But I must do my best, and leave the authors of the book and the readers of this journal to complain to the Editor of my inevitable deficiencies.

The difficulty in writing a book on photoelectric cells is that the audience addressed is so indeterminate. It is almost impossible to cater in a single volume for the pure theorist, the manufacturer, the experimenter, the engineer, the picture-telegraphist and talking film expert—and lastly the omnivorous person prepared to read about anything that he thinks new. There are only two alternatives open. One is to cater for all readers; the other to cater definitely for a single class and to neglect steadfastly all the rest. This second alternative is not as easy as it sounds; for the spheres of interest of different classes overlap, and the author, having entered a sphere in the interest of one class, is apt to explore it too far in the interests of another. Certainly neither Zworykin and Wilson nor Campbell and Ritchie have wholly mastered the difficulty; perhaps that is why Drs. Simon and Suhrmann have preferred the first alternative.

For both their preface and their list of contents indicate that their aim is to be encyclopaedic. They take credit that they have dealt much more fully than our books with theory, with manufacture, and with apparatus auxiliary to photoelectric research, and yet they have not abandoned wholly any of the matters with which we dealt; their section-headings cover every subject suggested by their title. As an encyclopedia then I propose to judge the book.

The merits required of an encyclopedia are completeness and accuracy. Let us test it on this score. Here is a list of the more important matters omitted. In their theory there is no mention of quantum mechanics. In methods of manufacture there is no hint of how to prepare the type of cell that now forms 90% of the output of "alkali metal" cells, at least in America and England. In fact I am not sure that this cell is even mentioned (for it is not always clear what a "caesium" cell means), although its cathode, produced by heating oxidised Ag in Cs vapour, is much more sensitive to white light than any other. There is no account of the selenium "Sperrschicht" cell, although it seems likely to replace the cuprous oxide cell to which many pages are devoted. For the cathode of cells to measure "erythema radiation" there is no mention of Li or Ur, both of which are claimed to be vastly superior to Cd, which they recommend. Under sources of ultra-violet light they mention neither the continuous H₂ spectrum or that of bombarded Th. "295 Abbildungen in Text" (including one photograph of a stop-watch and two of monochromators) are poor consolation for these omissions.

Inaccuracy in major matters is more difficult to establish; for authors so eminent as these are not likely to make mere blunders in strictly scientific matters. But in many cases conciseness seems to me pushed to the point where it becomes very misleading. But it is sometimes said: Inaccurate in one thing, inaccurate in all; let us test a minor matter then. The footnotes of the book are full of the orthodox "references," tabulated in the name-index. I naturally turn to my own name. 6 entries here. Of these one confuses me with Campbell-Swinton, who is not tabulated; another refers to a diagram, due to Clayton Sharpe, and representing an arrangement against which I have always mildly protested. 33% errors at a random trial.

Truly and honestly I should like to find countervailing virtues on which I could descant. One undoubtedly there is. Being the latest book, it is more up-to-date than any other; it includes, for instance, something about the very important Sperrschicht cells, which the older books hardly mention. But there my list ends. Lucidity cannot be included, and many readers will feel diffident about critical judgment when they observe how much space is given to the authors' own work. However all this is doubtless due to my prejudice—and so I had better stop. Since I wrote this Hughes and Du Bridge's book has appeared!

Norman R. Campbell

Hydrogen Ions. By F. T. S. Britton. 22 × 14 cms. Pp. xvi + 589. London: Chapman and Hall, 1932. Price: 52 shillings. That a second edition of Dr. Britton's work on hydrogen ions should be called for in less than three years after the appearance of the original edition, is, in itself, evidence of the popularity and merit of the book. The book deals with acid and alkali titrations and p_H measurements by the potentiometric and indicator method. Full accounts are given of the theoretical and practical details of both methods. The importance of p_H measurements in many industries (leather manufacture, chrome and mineral tanning, vegetable tanning, sugar manufacture, pulp and paper manufacture, brewing, baking, water purification, and soil fertility) is described at great length. The new edition is some 74 pages larger than the original edition, which is mainly due to the inclusion of new chapters on (i) "Recent theories of electrolytic solutions. The influence of neutral salts," (ii) The precipitation of sulphides, (iii) The hydrogen ion concentration of eggs. The new thermionic value circuits of Stadie, Harrison and others for potentiometric titration are described in detail. These circuits overcome the uncertainties found in the original method of Goode. The Harrison system of value amplification by means of which the E.M.F. of high resistance glass electrodes can be measured with a galvanometer is also clearly described. The theories of Lewis, Debye, Hückel, Harned and others on ion activities and electrolytic solutions are summarised and discussed. The author has also added to the account of his own work on buffer mixtures, and also on the antimony, antimony oxide, tungsten and oxygen electrodes. An account is also given of the importance of hydrogen ion concentration in the precipitation of hydroxide and basic salts. Much of the work described here is due to the author and his collaborators; it is fundamental, interesting and of great practical importance. An important error has however crept in on p. 303, Table 83a. A list of solubility products of hydroxides calculated from the precipitation curves depicted on p. 301 is given. The method of calculation is quite inaccurate, but the rather amazing fact is that the calculated values of the solubility product are generally in fair agreement with the values recorded in the literature.

Apart from the blemish noted above the book is very good. It gives a really good account of the theory and technique of hydrogen ion determination. It is well-balanced and it is written in a pleasant and readable manner, it is well illustrated and indexed. It is a book which may be warmly recommended.

James F. Spencer

Experimental Cookery. By Belle Lowe. 23 × 16 cm; pp. xi + 498. New York: John Wiley and Sons; London: Chapman and Hall, 1932. Price: \$4.50. A quotation of Ostwald's which Dr. Lowe has used in her introductory chapter concerning the relation of cookery to colloid chemistry is of such interest that I shall repeat it here. "Scientific study of the field still contents itself with chapters on analysis and the recognition of adulterants, but chapters dealing with the preparation of food are hardly started. Much as everyone would like to obtain better food for less money, study of such questions is regarded as menial and best left to the cook. A scientific study of the preparation of food is considered as only amusing even in scientific circles." These remarks were made in 1922.

The appearance of Dr. Lowe's book has supplied the *amused* scientist with information which is both obtained by and explained soundly on generally accepted colloidal principles. He may well stop being amused and devote himself to an interested study of the material she has presented. There are many of us who openly rejoice to have this material between two covers. No longer will certain classes need to grumble for an adequate text-book.

The arrangement of the book is logical and commendable; yet it is not necessary for the material to be used in just such a sequence. In the first chapter the author seeks to acquaint the student with the principles of colloidal chemistry which are of importance in the study of foods and food preparation. Unfortunately the majority of students in Home Economics have not had courses in even elementary Physical or Colloidal Chemistry; hence the tremendous importance of this first chapter. It is not a long chapter. After a general classification of substances based upon the degree of dispersion in solution, methods of lessening or increasing the degree of dispersion of substances in food preparation are dis-

cussed. Under the heading of Properties and Classes of Colloids based upon Physico-Chemical Relationships in Liquids, we find adequate discussion of reversible and irreversible colloids, colloid gels, swelling of gels, syneresis, coagulation of proteins, etc. In addition the chapter includes a discussion of boundary phenomena; fluidity, viscosity and plasticity of colloidal systems; energetics; and finally hydrogen ion concentration. It is an excellent summary—yet, as the author suggests, for the uninitiated student it would be a difficult chapter to digest. Either much lecture material must accompany its assimilation, or it should be, and probably better, utilized along with other chapters concerned with descriptive information regarding food and food manipulation. Otherwise such words as “cata-phoresis” may be difficult, and the importance of adsorption may be underestimated. There are many apt examples selected for each of the subjects included.

Other chapters in the book have to do with sugar cookery, freezing and the freezing process, fruits and vegetables, jelly, gelatin, meat, emulsions, milk, egg cookery, wheat flour and bread, batters and doughs, and fats and oils. At the conclusion of each chapter there is an ample and well worked out group of pertinent experiments.

The preceding list of subjects covered in the various chapters indicates that the book is comprehensive. The chapter concerned with batters and doughs is of such excellence that it may be considered separately. Leavening agents are considered first, then the structure of batters and doughs. There follow specific remarks concerning the formation and structure of popovers, timbales and cover batters, cream puffs, griddle cakes, waffles, muffins, biscuits and cakes. The information is well arranged and extensive. The illustrations in this particular chapter consist of diagrammatic drawings, photographs and photomicrographs, each one carefully labelled and serving as evidence for some well-made point.

The photomicrographs moreover, showing the size and appearance of sugar crystals in fondants made by various methods, and standing over varying time intervals, as well as those concerned with emulsions made by varying the quantities of oil and vinegar are unusually helpful. Surely the microscope is one of the most useful instruments for such studies and the permanent records obtained easily via its camera attachments are becoming invaluable aids to the chemist.

Another tremendously desirable feature of the book is the accommodating list of references following each chapter—lists commodious, yet at the same time sufficiently abridged to form a most useful compendium.

It is perhaps unwise and unfair for me to select certain parts for a more detailed comment than the others. Such is not my intention. The book is the work of an expert—assisted by experts; and represents another combination of essential chemistry with facts. Such are welcome additions to our literature.

Irene H. Sanborn

Solutions superficielles. *Fluides à deux dimensions, et Stratifications monomoléculaires.* By André Marcelin. 24 × 16 cm; pp. 163. Paris: Les Presses Universitaires de France, 1931. Price: 80 francs. M. Marcelin's volume is exactly described by its title and sub-title and represents a most valuable contribution to a subject which is, in many aspects, new and expanding, and which, moreover, has not been the subject of many monographs.

The author's development of the subject opens with a historical exposé, which, beginning with the fundamental observations of Miss Pockels, leads up to the developments made by Langmuir. He then proceeds to discuss the physical state of “solution superficielle,” following this by a detailed and very useful account of the experimental methods employed. Space will hardly permit even of the mention of the titles of all the sixteen chapters of the book, but we may say that no point of outstanding interest is omitted, and that, among other matters, we find a full treatment of oleic acid and of the dimensions of its molecule, of pseudo-superficial solution, of applications of the Gibbs equation, of the effect of a surface film in lowering the Volta effect between an electrotpe and a metal, and of black spots on films and of the thickness of *p*-toluidine crystals formed by solution or by sublimation.

M. Marcelin's clear and ordered account of the subject is very welcome and should find a place on the shelves of every physicist and chemist interested in the general properties of matter.

A. Ferguson

IRREVERSIBLE PROCESSES IN ELECTROLYTES. DIFFUSION, CONDUCTANCE, AND VISCOUS FLOW IN ARBITRARY MIXTURES OF STRONG ELECTROLYTES*

BY LARS ONSAGER AND RAYMOND M. FUOSS

1. Introduction

1.1. *Scope and Aims.*

In an electrolyte, the Coulomb forces between the ions will affect the thermodynamic and other physical properties of the system; these effects can be calculated, because the force law is known. The mathematical difficulties involved were first overcome by Debye and Hückel,¹ who derived limiting laws for the variation of molecular freezing-point depression, etc., and of molecular conductance with the concentration, c , all of the form

$$F(c) = F(o) - \alpha\sqrt{c} \quad (1.1.1)$$

where $F(c)$ stands for any one of these properties, while $F(o)$ and α are constants. The term $-\alpha\sqrt{c}$ represents the influence of the ionic forces. It is characteristic of the theory that the factor α can be computed. For functions $F(c)$ describing irreversible processes, the value of α will in general depend on the (limiting) ionic mobilities; in addition, only the charges of ions and the ratios of their concentrations are involved, besides properties of the solvent (and universal constants).

The present work deals with conductance, diffusion and viscosity; explicit formulas of the type (1.1.1) are derived. Earlier computations, which were limited to electrolytes containing only two species of ions, will be extended to electrolytes of arbitrary composition, although the scope of the investigation is still limited by the condition that *the total concentration of ions must be low*. As a consequence of mathematical approximations, we shall obtain in the end asymptotic formulas of the type (1.1.1), while more exact computations, which we have not attempted on account of the mathematical complications involved, would, judging from tentative calculations, lead to expressions of the type

$$F(c) = F(o) + \alpha\sqrt{c} + \beta c \log c + \gamma c + \cdots \quad (1.1.2)$$

The limiting \sqrt{c} laws for the conductance and transference numbers of *simple electrolytes* (i.e. containing only two species of ions), have been computed by one of us in a previous treatise,² which amounted to a refinement of the original theory given by Debye and Hückel.³

* Contribution from the Chemical Laboratory of Brown University.

¹ Debye and Hückel: I, *Physik. Z.*, **24**, 185 (1923); II, **24**, 305 (1923).

² Onsager: I, *Physik. Z.*, **27**, 388 (1926); II, **28**, 277 (1927).

³ Debye and Hückel: II, loc. cit.

The only published computations for electrolytes of a more general composition have been given by Bennewitz, Wagner and K  chler,¹ who considered the case of a third ionic species present in very small quantity.

Within the limited scope outlined above, the modern electrostatic theory of electrolytes has performed remarkably well in accounting for a complex pattern of experimental data on the basis of a simple picture.² The present calculations extend the range of phenomena thus covered. The most interesting effect connected with electrolytic conduction in mixtures, as contrasted to simple electrolytes, was first observed experimentally by Bray and Hunt,³ who measured the conductance of NaCl-HCl mixtures, and showed that the iso-ionic principle does not hold; that is, the conductances for a given total concentration of ions (and the same total "ionic strength") are not additive in this case. No corresponding effect is observed in the thermodynamic behavior of electrolytes, and curiously enough, the theory predicts for *simple binary electrolytes*, in accordance with an empirical rule due to Kohlrausch,⁴ that the mobility of any ion at a given concentration is independent of its partner ion in the solution, e.g., Λ_{Cl} is the same in 0.01 *n.* HCl as in 0.01 *n.* KCl. In a HCl-KCl mixture, as we shall see in the following, the theory predicts that the fast H^+ ions will be slowed down more than usual, while the slow K^+ ions, "stealing their thunder" as the ions migrate past each other, will be accelerated in proportion, and the Cl^- ions will move with (practically) their usual velocity. The nature of the effect was recognized by Bennewitz, Wagner and K  chler;⁵ it has been demonstrated experimentally by these authors and by Longworth.⁶ The present computations permit a quantitative comparison between theory and experiment. When due allowance is given for mathematical approximations, which become rather serious for, say, 0.1 *n.* concentration, the experimental verification may be called satisfactory.

The investigation of diffusion is possibly the most important part of the present contribution to the theory of electrolytes. Here the main effect of electrostatic forces between the ions is a thermodynamic one: The gradient of the thermodynamic potential, which represents the "driving force" upon the ions, is less than it would be in an ideal solution for the same concentration gradient.⁷ However, we shall see that the velocity of diffusion for a given "driving force" may also be affected by the electrostatic (and hydrodynamic)

¹ Bennewitz, Wagner and K  chler: *Physik. Z.*, **30**, 623 (1929).

² In this discussion we shall concentrate on the problem in hand, and make no pretense of doing justice to mass-action effects, or in general to specific interaction of ions. The procedure for taking such effects into account is fairly obvious; the questions involved have been taken up by several authors and have, by and large, been given adequate consideration. See N. Bjerrum: *Kgl. Danske Videnskab. Selskab. Math. fysis. Medd.*, VII, No. 9 (1926); Gronwall, LaMer and Sandved: *Physik. Z.*, **29**, 358 (1928).

³ Bray and Hunt: *J. Am. Chem. Soc.*, **33**, 781 (1911).

⁴ Kohlrausch and Holborn: "Leitverm  gen der Elektrolyte"; MacInnes and Cowperthwaite: *Trans. Faraday Soc.*, **23**, 400 (1927).

⁵ Bennewitz, Wagner and K  chler: *Loc. cit.*

⁶ Longworth: *J. Am. Chem. Soc.*, **52**, 1897 (1930).

⁷ At higher concentrations, where short range repulsive forces become noticeable, an increase may result. For thermodynamic properties of concentrated electrolytes, see Harned: *Trans. Faraday Soc.*, **23**, 462 (1927) and H  ckel: *Physik. Z.*, **26**, 93 (1925) (theory).

interaction of ions. Where more than two species of ions are present, the latter effects gain in importance (because the condition of zero electric current no longer forces all ions to move with the same velocity). Fundamentally, the problems of diffusion and conduction belong together; we thereby consider the most general migration of ions. From this point of view, the special case of pure conduction is not entitled to any preference. The general problem offers no additional obstacles to the theory; on the contrary, the essential characteristics of the problem are more readily recognized by avoiding an unnatural specialization.

The most general description of the laws of diffusion (and conduction) in a multi-component system will be formulated. The theory of electrolytes furnishes a good example in that all the terms in the phenomenological equations are important. We shall only be concerned with the formulation of the differential equations, which even for a simple electrolyte lead to a variable constant of diffusion, and make no attempt to integrate them for any practical case. For an actual test of the theory it would seem necessary to carry out experiments in which the difference between the concentrations of the inter-diffusing solutions were relatively small, so as to measure the *differential* coefficient of diffusion, which is considered by the theory.

The differential equations for diffusion take the simplest form when expressed in terms of "driving forces," namely the gradients of thermodynamic potentials.¹ A system of linear equations

$$-J_i = \sum_{k=1}^s \Omega_{ik} \text{grad } \mu_k, \quad (i = 1, 2, \dots, s), \quad (1.1.3)$$

relate the velocities v_1, \dots, v_s (relative to the solvent) of the different ionic species to the gradients of the *total potentials*

$$\mu_i = \mu'_i + e_i \psi, \quad (1.1.4)$$

where μ_i is the ordinary thermodynamic potential of Gibbs, ψ the electrostatic potential, and e_i is the charge per unit amount of a species of ions. As pointed out by Guggenheim and others,² only the sum (1.1.3) enters into thermodynamic relations, and into the laws of diffusion. The matrix Ω is symmetrical:

$$\Omega_{ik} = \Omega_{ki}. \quad (1.1.5)$$

This symmetry relation, which is responsible for a well-known relation between transference number and electromotive force of a concentration-cell with transference,³ is not a thermodynamic theorem,⁴ but it can be derived

¹ Cf. W. Nernst, who expressed the driving forces in terms of osmotic pressure, which is directly related to thermodynamic potentials. Nernst: *Z. physik. Chem.*, **2**, 613 (1888). The thermodynamic relations in question have been discussed by N. Bjerrum: *Z. physik. Chem.*, **104**, 406 (1923).

² Guggenheim: *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540, 1758 (1930); *J. Am. Chem. Soc.*, **52**, 1315 (1930); P. B. Taylor: *J. Phys. Chem.*, **31**, 1478 (1927).

³ H. v. Helmholtz: *Wied. Ann.*, **3**, 201 (1876); *Wiss. Abh.* **1**, 840; MacInnes and Beattie: *J. Am. Chem. Soc.*, **42**, 1117 (1920).

⁴ Cf. J. W. Gibbs: "Collected Works" **I**, 425 (1928); W. D. Bancroft: *J. Phys. Chem.*, **7**, 416 (1903).

from the very reasonable assumption that molecular dynamical systems, like those known to our macroscopic experience, possess symmetry in past and future.¹

The following computations will be based on certain fairly general assumptions regarding the mechanism of resistance to migration of ions. The assumed mechanism is compatible with the principle of microscopic reversibility, and, as one should expect, the results conform to (1.1.5). An alternative form of (1.1.3), incorporating the symmetry relation (1.1.5), is obtained by the construction of a "dissipation-function."

The problem of viscosity has been included in this treatise mainly because it yields to the same mathematical methods as the conductance-diffusion problem; we thereby avoid a duplication of the calculations, which are to a great extent identical for both problems. The electrostatic contribution to the viscosity η of an electrolyte obeys the formula

$$\eta(c) - \eta(0) = \alpha\sqrt{c}, \quad (1.1.6)$$

as has been shown by earlier calculations and experiments² by other authors for simple electrolytes. In extending the theory to cases where 3 or more species of ions are present, we find that no new spectacular effects are to be expected. In some respects, the present treatment of the viscosity problem brings simplification as compared to previous computations. In regard to the physical picture, we disagree with Falkenhagen³ on one detail which, fortunately, does not affect the result for viscosity. He considers cases where the velocity gradients for the ions differ from the gradient for the solvent and, in our opinion, a material difference cannot occur. Falkenhagen arrived at his conclusion in searching for a mechanism of force transfer between ions and solvent. We have therefore investigated the mechanism of force transfer, an interesting problem in itself (although a barren one for experimenters), and we can show that there must indeed be a motion of ions relative to the solvent, but of another type than that suggested by Falkenhagen: The transfer of force that takes place in any given volume element, and consequently the local flow density of ions relative to the solvent, will be *proportional to the divergence of the velocity gradient*. In addition, there may be a transfer of force in the boundary layer; in the simplest case of a constant velocity gradient, the entire transfer of force takes place along the boundary.

1.2. *Present and Possible Future Advances in Mathematical Methods.*

In the present work, certain mathematical methods which are well known to other branches of theoretical physics will be applied for the first time to the theory of electrolytes. On this basis alone a brief survey of mathematical methods seems advisable and we have another, more important reason: while the scope of the present computations will be limited so as to obtain only the

¹ Onsager: *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).

² Grinnell Jones and M. Dole: *J. Am. Chem. Soc.*, **51**, 2950 (1929); Falkenhagen and Dole: *Z. physik. Chem.*, **6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929); Falkenhagen: *Physik. Z.*, **32**, 365, 745 (1931).

³ Falkenhagen: *Physik. Z.*, **32**, 365 (1931).

first (\sqrt{c}) term of the expansion (1.1.2) correct, we believe that a refinement of these calculations would be practicable, though laborious, and we have definite ideas about the procedure.

The computation consists of two parts: first (in section 2), the derivation of fundamental equations for the "ionic atmospheres," simplified by certain approximations, and, second (in sections 3 and 4), the specialization and the solution of the fundamental equations for the different cases to be considered, namely the problem of viscosity and that of conduction and diffusion.

The derivation of the fundamental equations will be complete in itself, and accessible to a reader familiar with the theory given by Debye and Hückel for the thermodynamic properties of electrolytes, which comprises the "statics" of the ionic atmosphere. We believe that a certain measure of simplification as compared to a previous treatise¹ will be welcome.

Full mathematical rigor is a distant ideal for the theory of electrolytes, but in our opinion, some advances towards this ultimate goal are possible.² It is already very difficult to justify rigorously inevitable approximations, and to establish an upper limit for the error thus introduced. The "static" theory of an electrolyte in thermodynamic equilibrium has been carried further,³ but even there, the so-called "fluctuation-terms" in the differential equations are neglected,⁴ and the effect of these terms is very difficult to estimate. Tentative calculations of our own tend to show that the "fluctuation-terms" are of minor importance, but it would be necessary to go more carefully into the question.

For the time being, it would be a great advance, in a certain sense a completion of the electrostatic theory (dealing only with Coulomb forces), if a method could be devised to compute the fields of the "ionic atmospheres" by a series of successive approximations, making it reasonably certain that the method would converge to the desired result, even though a mathematical proof of the convergence might be too much to ask.

In this sense, the original calculations of Debye and Hückel, and for the theory of irreversible processes those of the present work, may be considered as a first step in a series of approximations, which proceeds by developing the potential in the neighborhood of one particular ion, or a pair, triple, etc. of ions⁵ in a power series of its charge (their charges). The distribution-functions can likewise be developed in power series. The two sets of functions are combined (in the "static" case) by the Boltzmann principle and the Poisson equations, and the terms in the power series can be calculated successively, whereby each

¹ Onsager: *Loc. cit.*

² We are only concerned with the mathematical aspects of the derivation, and not as yet with the question of designing a physical picture that will account properly for all experimental results. Until we have a mathematically reliable theory, leading to definite conclusions on the basis of a reasonable picture, we do not know whether the experiments test the physical picture or merely our mathematical dexterity, or possibly a deceptive compensation of both.

³ Gronwall, LaMer and Sandved: *Physik. Z.*, **29**, 358 (1928).

⁴ R. H. Fowler: *Trans. Faraday Soc.*, **23**, 434 (1927); L. Onsager: *II*, *loc. cit.*

⁵ By considering the neighborhoods of pairs, triples, etc. of ions, it is possible to evaluate the fluctuation terms.

new term may add corrections to the preceding. This method looks promising from the point of view of convergence, because the functions to be calculated, qua functions of the charges, are probably entire functions, whose series converge like e^x . It also seems probable that the method can be generalized to deal with irreversible processes, whereby the equation of continuity, which is the condition for a stationary state (in a statistical sense), replaces the Boltzmann principle. In applying this method of computation to electrical conduction, a complication arises because the external force on an ion is proportional to its charge. The complication is only apparent, and may be disposed of by replacing the electrostatic force temporarily by an arbitrary field of forces, which is not supposed to be a function of the charge, until the necessary approximations have been made. This procedure, which will be employed in the following, is necessary in order that the simplicity and the self-consistency of the principle of approximation become evident. As a further means of emphasizing the uniform character of the calculations, all approximations will be introduced before specialization to particular problems: viscosity and conduction + diffusion. In fact, a starting-point for calculating conductance in strong electric fields (Wien-effect), as given by Joos and Blumentritt,¹ may be found in our (2.5.7), which contains the approximations referred to, but which is not as yet specialized for weak fields. Likewise, the dispersion of conductance, as calculated by Falkenhagen, may be obtained from our calculations by retaining in the equation of continuity the left-hand member $\partial f / \partial t$ (instead of 0), throughout the derivation.

In order to obtain a wieldy *solution* of the differential equations for the ionic atmospheres, we shall introduce matrix notation. Once this powerful mathematical tool is applied, we can deal with a system of linear differential equations as if it were one, and the intended generalization from an electrolyte containing only 2 species of ions to the case of s species becomes practically trivial. Moreover, this is the only way to obtain solutions that are formally compact, and even the methods for a *numerical computation* are most easily derived from the final results as they appear in matrix notation.

For a possible future refinement of the calculations along the lines indicated above, it will be necessary to know the solution of the equations that appear in the first approximation for the general case of s ions, because the principle of the method is to develop the potentials, etc. pertaining to each ionic species in power series of their charges, which implies variable charge and therefore variable species. (In order to accomplish anything with the fictitious ions involved in this method of computation, we must be able to deal with real ones.)

1.3. *Outline of the Physical Picture.*

As shown by Debye and Hückel, the effects of the Coulomb forces between the ions on the properties of electrolytes depend on the electric forces preventing a random arrangement of the ions in the solution. Instead, each positive

¹ Joos and Blumentritt: *Physik. Z.*, **28**, 836 (1927); Compare also Falkenhagen: *Physik. Z.*, **32**, 353 (1931).

ion will surround itself with an "atmosphere" containing on the average more negative ions and less positive ions than the bulk of the solution, thus inducing a negative charge density in its neighborhood, while a negative ion will surround itself with a positively charged "atmosphere."

The total (mean) electric charge of an ionic atmosphere equals that of the central ion, with opposite sign, which suffices exactly to consume the force lines from the ion, so that its electric field beyond the bounds of the atmosphere is completely screened off.

The most important quantity characteristic of the ionic atmosphere is its mean radius, which can be calculated from the equilibrium between electric attraction and thermal agitation to be approximately $1/\kappa$ where

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{k=1}^s n_k e_k^2. \quad (1.3.1)$$

Here the electrolyte is supposed to contain ions of the species $1, \dots, s$ with the charges e_1, \dots, e_s in the concentrations n_1, \dots, n_s , while D denotes the dielectric constant, T the temperature, and k Boltzmann's constant, the gas constant per molecule. For the potential in the neighborhood of an ion of charge e , Debye and Hückel have derived the formula

$$\psi_j = \frac{e_j}{D} \frac{e^{-\kappa r}}{r} \quad (1.3.2)$$

which may be compared with $\psi = e/Dr$ for an isolated ion. According to (1.3.1), the inverse mean radius κ of the atmosphere is proportional to the square root of the concentration n , or exactly to

$$(\sum n_i z_i^2)^{1/2}$$

where z_1, \dots, z_s are the valences of the ions; hence the frequent occurrence of the power $n^{1/2}$, as in (1.1.1), in the theory of electrolytes. For instance, on the basis of (1.3.2), the potential at an ion due to its atmosphere will be

$$\psi_j = -\kappa e_j,$$

and this quantity determines the electrostatic contribution to the thermodynamic potential of an ion, which is

$$\Delta\mu_j = \frac{1}{D} \int_{\epsilon=0}^{\epsilon=e_j} \bar{\psi}(\epsilon) d\epsilon = -\frac{\kappa e_j^2}{2D}.$$

The numerical value of κ for a univalent binary electrolyte in water at 291° abs. amounts to

$$\kappa = 0.332 \times 10^8 \sqrt{c}$$

where c is the concentration in mols/liter. Thus for $c = 0.1$, $1/\kappa = 10^{-7}$ cm. and for $c = 1$, $1/\kappa = 3 \times 10^{-8}$ cm.

Two other quantities of the dimension length are of interest in the theory of electrolytes, namely the diameter a of an ion, for small univalent ions in water usually in the range

$$2 \times 10^{-8} < a < 4 \times 10^{-8} \text{ cm,}$$

and the distance

$$d_0 = e^2/DkT, \quad (1.3.3)$$

at which two ions of charge e have the mutual potential energy kT . For univalent ions in water, approximately,

$$d_0 = 7 \times 10^{-8} \text{ cm.}$$

The approximations employed in the following computations, as well as (1.3.2), will be admissible¹ as long as the radius $1/\kappa$ of the ionic atmosphere is large compared to a and d_0 ; according to (1.1.1), this is indeed the case for sufficiently low concentrations. It is seen from the numerical data given above that for a univalent binary electrolyte in water, $1/\kappa = d_0$ for a molar concentration $c = 0.2$ and $1/\kappa = a$ for a concentration c near 1.0.

We shall discuss one more quantity of general interest pertaining to the ionic atmospheres, namely the *time of relaxation*. The importance of this quantity for irreversible processes in electrolytes has been emphasized already by Debye and Hückel. When the ions in the electrolyte migrate under the influence of an electric field (conduction) or a concentration gradient (diffusion), the symmetry of the ionic atmospheres will be disturbed in a manner that one may visualize by considering one ion under the influence of an external force: The ion will try to run away from its atmosphere, which becomes asymmetric with respect to the central ion.

A *velocity gradient* present in a moving electrolyte will cause a somewhat different type of disturbance: In laminar motion, spheres are deformed into ellipsoids, and the ionic atmospheres will assume a corresponding asymmetry.

Now the "normal" structure of an ionic atmosphere is an equilibrium between electric forces and thermal agitation of the molecules. These agencies are continually operating, and will tend to restore equilibrium after every disturbance.

The *time* τ that is necessary for this process of *relaxation* is given by the linear dimensions of the region in question, here $1/\kappa$, and the coefficient of diffusion, which equals kT/ρ where ρ is the frictional force on an ion moving with unit velocity.

On the basis of the general equation for diffusion

$$\frac{\partial c}{\partial t} = \frac{kT}{\rho} \frac{\partial^2 c}{\partial x^2}$$

the time of relaxation becomes

$$\tau = \frac{(1/\kappa)^2}{(kT/\rho)} = \frac{\rho}{\kappa^2 kT} \quad (1.3.4)$$

¹ Our description of the part of the ionic atmosphere that is inside d_0 (and a) will be inaccurate; but as long as $1/\kappa \gg d_0$, the interior region ($r < d_0$) of the atmosphere is negligible compared to the rest. The approximations in question, which partly compensate each other, amount to neglecting higher terms in a power series expansion of $\exp(w/kT)$, where $w = e^2/Dr$ is the potential energy of a pair of ions, and in allowing impossible distances ($< a$) between ions.

except for a possible numerical factor of the order of magnitude unity. For the case of KCl in water at a temperature 291° abs. the above formula yields

$$t = \frac{0.55}{c} \times 10^{-10} \text{ sec.}$$

On account of this finite time of relaxation, a disturbance operating at a constant rate, such as migration of the ions, will maintain a constant deformation of the ionic atmosphere. On general principles, the resulting forces tend to oppose the causative disturbance; hence the Coulomb forces in the ionic atmospheres will yield contributions to the electrical resistance, the viscosity, etc., of the solution. The magnitude of such effects, and also of another effect, the "electrophoresis," which modifies the migration of the ions, will be discussed separately in dealing with the different phenomena. First, the fundamental equations for the process of relaxation will be derived.

2. Fundamental Equations for the Ionic Atmospheres

2.1. *The Distribution Functions.*

We are given a solution containing per cm^3 n_1, n_2, \dots, n_s ions of species 1, 2, . . . s with charges e_1, e_2, \dots, e_s e.s.u. per ion. Our problem is to find the limiting laws which describe an irreversible process such as electrolytic conductance, diffusion or viscous flow which may occur in the solution. The idea underlying the modern theory of electrolytes is that the presence of any particular ion at a given point in the solution will affect the chance of finding any other ion at a near-by point; in other words, the space distribution of ions cannot be entirely random as is presumably the case for an uncharged solute. We therefore shall need for our discussion a function which will give the chance of finding any two ions in two particular volume elements in the solution. This function may be specified by the following consideration.

Let two volume elements $dV_1 = dx_1 dy_1 dz_1$ and $dV_2 = dx_2 dy_2 dz_2$ in the solution be located by vectors \mathbf{r}_1 and \mathbf{r}_2 drawn from an arbitrary origin. (See Fig. 1). The second is then located with respect to the first by means of the vector

$$\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1 = -\mathbf{r}_{12} \quad (2.1.1)$$

(where the order of subscripts indicates the order of terms in the subtraction). For convenience in general discussions, we introduce for the components of \mathbf{r}_1 and \mathbf{r}_2 the notation

$$\begin{aligned} q_1^1 &= x_1, q_1^2 = y_1, q_1^3 = z_1 \\ q_2^1 &= x_2, q_2^2 = y_2, q_2^3 = z_2, \end{aligned} \quad (2.1.2)$$

and shall mean by q_1^k (q_2^k) either x_1, y_1 or z_1 (x_2, y_2 or z_2) according to $k = 1, 2, 3$. Then

$$q^k = q_{21}^k = q_2^k - q_1^k = -q_{12}^k \quad (2.1.3)$$

gives the coordinates of dV_2 with respect to an origin at dV_1 . We shall also need temporarily a symbol to denote any one of the six coordinates x_1, \dots, z_2 ; we shall use ξ_m for this purpose, where $m = 1, 2, \dots, \text{or } 6$.

We have postulated that the presence of an ion of a given species will affect the ionic concentrations in its vicinity; we indicate this explicitly by writing n_{ji} for the (time) average concentration of i -ions in the neighborhood of a j -ion. Now n_{ji} will in general depend on several variables, according to the situation to be investigated. (1) It will always depend on the distance r between the j -ion and the point where the concentration of i -ions is sought; (2) When forces act on the ions, a particular direction in space is specified,

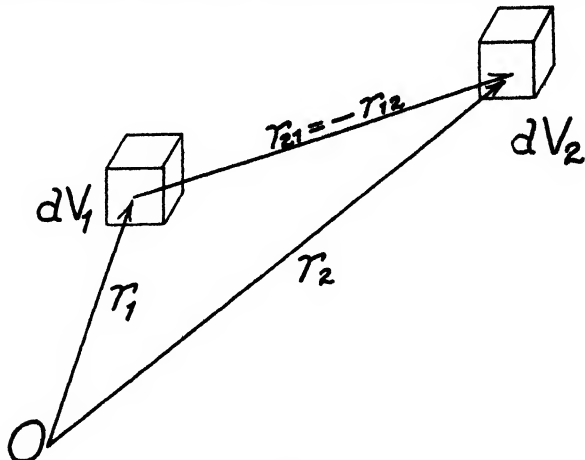


FIG. 1
Definition of Vectors

and n_{ji} will then depend on the direction of r ; (3) Finally, if a variable velocity gradient is present in the liquid (viscosity), n_{ji} will depend on the location of the j -ion. Therefore

$$n_{ji} = n_{ji}(\mathbf{r}_1, \mathbf{r}_{21});$$

and likewise,

$$n_{ij} = n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \quad (2.1.4)$$

gives the average concentration of j -ions at a distance $|\mathbf{r}_{12}|$ in the direction of \mathbf{r}_{12} from an i -ion located by \mathbf{r}_1 .

Now let us observe the pair of volume elements dV_1 and dV_2 ($\mathbf{r}_1, \mathbf{r}_2$ fixed temporarily) for a time t which is large compared to the time involved in the Brownian movement of the ions. We confine our attention to any two particular species of ions, say i and j . Our observations are made by means of three hypothetical clocks A , B , and C . Clock A starts each time a j -ion enters dV_1 , and stops when the ion leaves so that the total time t_j recorded is the sum of the intervals out of the total observation time t during which a j -ion actually is in dV_1 . Clock B starts when an i -ion enters dV_2 , and stops when it leaves, and thus records the time t_i during which an i -ion actually is present in dV_2 . Clock C starts when an i -ion enters dV_2 while a j -ion is in dV_1 or when a j -ion enters dV_1 while an i -ion is in dV_2 , and stops when either ion leaves the corresponding volume element while the other ion remains in its element. Clock C thus records the time t_{ji} common to t_i and t_j , so that

t_{ji} is the total time out of t during which we simultaneously have a j -ion in dV_1 and an i -ion in dV_2 . We then use the results of our experiment to compute the concentrations as time averages. We obtain

$$\begin{aligned} t_j/t &= n_j dV_1, \quad t_i/t = n_i dV_2; \\ t_{ji}/t_j &= n_{ji} dV_2, \quad t_{ji}/t_i = n_{ij} dV_1. \end{aligned}$$

Eliminating t_j and t_i , we have

$$t_{ji}/t = n_j n_{ji} dV_1 dV_2 = n_i n_{ij} dV_2 dV_1. \quad (2.1.5)$$

We may then use the relationship expressed in (2.1.5) to define our distribution functions, since they give the chance of finding simultaneously a j -ion in dV_1 and an i -ion in dV_2 . Accordingly, we write

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_j n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_i n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}). \quad (2.1.6)$$

We can now make more precise our picture of interionic action, supposing for a moment that a positive ion is fixed in dV_1 . Then on the average, negative ions will enter dV_2 more frequently and therefore be present for a greater fraction of the total time, while positive ions will be scarce; this excess of negative ions persisting around the positive ion forms the so-called ionic atmosphere. In an undisturbed electrolyte, the atmosphere is obviously central-symmetric.

2.2. The Equation of Continuity.

We shall next investigate how f changes with time.¹ In order to consider this problem conveniently we plot in 6-dimensional space the coordinates ξ_1, \dots, ξ_6 , so that specifying a point in 6-space specifies a pair of points in the solution, i.e., we can follow the behavior of dV_1 and dV_2 simultaneously by observing the volume element $d\xi_1 \dots d\xi_6$. If we designate by \mathbf{v}_i the velocity of an i -ion in the vicinity of a j -ion, then

$$\mathbf{v}_{ji} = \mathbf{v}_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \quad (2.2.1)$$

will in general depend on the location of both ions as well as on the location of the i -ion relative to the j -ion. Likewise,

$$\mathbf{v}_{ij} = \mathbf{v}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}).$$

The average components of velocity of a j -ion in dV_1 are ξ_1, ξ_2, ξ_3 and of an i -ion in dV_2 ξ_4, ξ_5, ξ_6 in 6-space. Now let us consider a 6-dimensional cube, whose center is at ξ_1, \dots, ξ_6 and whose sides are of length $\Delta\xi_r$ ($r = 1, \dots, 6$). Then if ξ_r is the r -th component of velocity at the center of the cube and $f_{ji}(=n_j n_{ji})$ is the concentration (in 6-space) at the same point, the flow of ions through a 5-dimensional face of the cube of area ΔS_r perpendicular to the ξ_r axis is

$$\left\{ \xi_r f_{ji} \pm \frac{\partial(\xi_r f_{ji})}{\partial \xi_r} \frac{\Delta \xi_r}{2} \right\} \Delta S_r,$$

¹ The meaning of $\partial f / \partial t$ may seem obscure, since f is already defined as a time average. However, we may still ask for the "secular" change of this average in the course of a relatively long time. For the consideration of rapid changes (variation of conductance with frequency) the function f must be re-defined as an average over many similarly situated pairs of volume elements. Cf. Debye and Falkenhagen: *Physik. Z.*, 29, 401 (1928).

so that the difference between influx and outflow for any pair of faces of the cube is $-\frac{\partial(\xi_r f_{ji})}{\partial \xi_r} \Delta \xi_r \Delta S_r$ per unit time. Obviously $\Delta \xi_1 \dots \Delta \xi_6 = \Delta \xi_r \Delta S_r$.

Then the total contribution of all 6 pairs of faces gives the time change of concentration in the volume element

$$\frac{\partial f_{ji}}{\partial t} \Delta \xi_1 \dots \Delta \xi_6 = - \sum_{r=1}^6 \frac{\partial(\xi_r f_{ji})}{\partial \xi_r} \Delta \xi_r \Delta S_r. \quad (2.2.2)$$

Dividing out the volume element, we have the equation of continuity, where the differentiation on the right gives a 6-dimensional divergence. But

$$\sum_r \frac{\partial}{\partial \xi_r} = \text{div}_1 + \text{div}_2,$$

where the subscripts 1 and 2 refer respectively to differentiation with respect to the components of \mathbf{r}_1 and \mathbf{r}_2 . Since $f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})$ by (2.1.6), and ξ_1, ξ_2, ξ_3 (ξ_4, ξ_5, ξ_6) are the components of \mathbf{v}_{ij} (\mathbf{v}_{ji}), (2.2.2) may be written

$$-\frac{\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t} = \text{div}_1 (f_{ij} \mathbf{v}_{ij}) + \text{div}_2 (f_{ji} \mathbf{v}_{ji}) = -\frac{\partial f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})}{\partial t} \quad (2.2.3)$$

In any steady state, f is independent of time so that we obtain the stationary condition that

$$\text{div}_1 (f_{ij} \mathbf{v}_{ij}) + \text{div}_2 (f_{ji} \mathbf{v}_{ji}) = 0. \quad (2.2.4)$$

2.3. The Equations of Motion.

In our problems, three effects contribute to the motion of the ions: (1) forces on the ions, (2) thermal motion, (3) flow of the solution itself. If $\rho_i = 1/\omega_i$ is the friction coefficient of an ion of the i -th species, then a force \mathbf{K}_i gives the ion a velocity $\mathbf{K}_i \omega_i$. We shall use the generalized equation¹ for Brownian movement to calculate the velocity due to thermal motion. The diffusion constant is assumed to be $kT\omega$ so that a concentration gradient will cause a current of strength $-kT\omega \text{ grad } f$. Then the average diffusion velocity is $-kT\omega \text{ grad } \ln f$. If the bulk velocity of the solution at the point located by \mathbf{r}_2 is $\mathbf{V}(\mathbf{r}_2)$, then

$$\mathbf{v}_{ji} = \mathbf{V}(\mathbf{r}_2) + \omega_i(\mathbf{K}_{ji} - kT \text{ grad}_2 \ln f_{ji})$$

gives the total velocity \mathbf{v}_{ji} which appears in (2.2.4). We have written \mathbf{K}_{ji} for the (mean) force which acts on an i -ion in the vicinity of a j -ion.

The equation of continuity specialized for a steady state now takes the form

$$\begin{aligned} & \text{div}_1 \{f_{ij} \mathbf{V}(\mathbf{r}_1) + \omega_j(f_{ij} \mathbf{K}_{ij} - kT \text{ grad}_1 f_{ij})\} + \\ & \text{div}_2 \{f_{ji} \mathbf{V}(\mathbf{r}_2) + \omega_i(f_{ji} \mathbf{K}_{ji} - kT \text{ grad}_2 f_{ji})\} = 0, \end{aligned} \quad (2.3.1)$$

where

$$\begin{aligned} f_{ji} &= f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), & f_{ij} &= f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \\ \mathbf{K}_{ji} &= \mathbf{K}_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), & \mathbf{K}_{ij} &= \mathbf{K}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}). \end{aligned}$$

¹ Debye and Hückel: II, loc. cit.

² We here neglect the hydrodynamic motion of the fluid at dV_1 caused by the presence of a moving j -ion at dV_1 . This approximation amounts to dropping terms of the order $c \log c$ in the final results.

2.4. The Results of Debye and Hückel for an Undisturbed Electrolyte.

For the case of an electrolyte at rest under the action of no external forces, the ionic atmospheres are spherically symmetric with respect to the central ion, and the functions introduced above become pure functions of the distance $r = |\mathbf{r}_{21}| = |\mathbf{r}_{12}|$. We therefore write

$$f_{ji}^{\circ}(r) = n_j n_{ji}^{\circ}(r) = n_i n_{ij}^{\circ}(r) = f_{ij}^{\circ}(r) \quad (2.4.1)$$

to indicate this situation.

An ion of charge e_j in a liquid of dielectric constant D produces a field derivable from the potential

$$e_j/Dr.$$

In an electrolytic solution, the fields due to the various ions superpose and any particular ion will be screened by the ions in its atmosphere. We designate by $\psi_j(\mathbf{r}_1, \mathbf{r}_{21})$ the potential due to an ion and its atmosphere in the general case and by $\psi_j^{\circ}(r)$ the same for the undisturbed case. The potentials are connected with the charge density

$$\sum_i n_i e_i$$

by the Poisson equations

$$\Delta\psi_j = -\frac{4\pi}{D} \sum_i n_i e_i \quad (2.4.2)$$

$$\Delta\psi_j^{\circ} = -\frac{4\pi}{D} \sum_i n_i^{\circ} e_i. \quad (2.4.3)$$

If we assume that the concentration n_{ji}° of i -ions near a j -ion is determined from the energy¹ E_{ji} of an i -ion in the vicinity of a j -ion by the Maxwell-Boltzmann distribution, we have

$$n_{ji}^{\circ} = n_i \exp(-E_{ji}/kT). \quad (2.4.4)$$

For this equilibrium, the average velocities must vanish, so that

$$\mathbf{K}_{ji} = \mathbf{K}_j = kT \text{ grad } \ln f_{ji}^{\circ}. \quad (2.4.5)$$

From (2.4.4), we find

$$kT \text{ grad } \ln f_{ji}^{\circ} = -\text{grad } E_{ji} = -\text{grad } E_{ij}. \quad (2.4.6)$$

So far, no approximation has entered. If now we assume *linear* superposition of the potentials and consequently of the charge densities induced by two ions near one another (superposition of the atmospheres), we assume that $E_{ji} = e_i \psi_j^{\circ}$ and $E_{ij} = e_j \psi_i^{\circ}$. In other words, the average force acting on one ion is given by the potential of the atmosphere of the other. Then from (2.4.6), we see that our assumption leads to the result that

$$e_i \psi_j^{\circ} = e_j \psi_i^{\circ}$$

¹ E_{ji} is most simply defined by $\mathbf{K}_{ji} = -\text{grad } E_{ji}$ to be the potential of the force \mathbf{K}_{ji} ; according to (2.4.5), this force has indeed a potential. It is also possible to define E_{ji} as the net work of discharging an i -ion far away from the particular j -ion under consideration, moving it (without work) into the atmosphere of that j -ion, and recharging the i -ion at the distance r .

which means that the potential around an ion must be *proportional* to its charge;

thus
$$\psi_j^\circ = e_j F(r)$$

where $F(r)$ is independent of e_j . On the other hand, if we substitute $E_{ji} = e_i \psi_j^\circ$ into (2.4.4) and the latter into (2.4.3), we find

$$\Delta \psi_j^\circ = -\frac{4\pi}{D} \sum_i e_i n_i \exp(-e_i \psi_j^\circ / kT)$$

but here, by hypothesis, the left member is linear in e_j while the right member evidently is not; hence our assumption has led to a contradiction. However, for small values of $e_i \psi_j^\circ$ we have

$$\exp(-e_i \psi_j^\circ / kT) \approx 1 - e_i \psi_j^\circ / kT \quad (2.4.7)$$

approximately, and if we allow this approximation, we obtain the linear equation

$$\Delta \psi_j^\circ = \kappa^2 \psi_j^\circ \quad (2.4.8)$$

where

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{i=1}^s n_i e_i^2. \quad (2.4.9)$$

The error which arises from terminating the power series for the exponential is small at great distances from the (j) ion, since ψ_j° is small. In the immediate vicinity of the central ion, namely for

$$r \leq d_0 = e_j e_i / DkT$$

(cf. 1.3.3), the approximation is poor. However, for *low concentrations*, the radius $1/\kappa$ of the ionic atmosphere, which, according to (2.4.9), varies as $c^{1/2}$, becomes large and for $1/\kappa \gg d_0$ the inaccurate description of the innermost region will cause a negligible error in our final results. Integration of (2.4.8) yields, considering the boundary conditions,

$$\psi_j^\circ = \frac{e_j}{D} \frac{e^{-\kappa r}}{r}. \quad (2.4.10)$$

This procedure was developed by Debye and Hückel. With the above approximation (2.4.7), the distribution function becomes

$$\begin{aligned} f_{ji}^\circ &= n_j n_i^\circ = n_j n_i (1 - e_i \psi_j^\circ / kT) = \\ &= n_j n_i \left(1 - \frac{d_0 e^{-\kappa r}}{r} \right) = n_j n_i \left(1 - \frac{e_j e_i}{DkT} \frac{e^{-\kappa r}}{r} \right). \end{aligned} \quad (2.4.11)$$

2.5. Perturbation of the Ionic Atmospheres.

If a force acts on the ions in the solution under investigation, then there exists a preferred direction, and both distribution functions and potentials become asymmetric. We shall assume that the applied forces are small, so that we may consider the various functions to be changed by a small perturbation factor from their values in the undisturbed electrolyte. Accordingly, we set

$$\psi_j = \psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) + \psi^\circ_j(r) \quad (2.5.1)$$

$$f_{ji} = f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) + f^\circ_{ji}(r). \quad (2.5.2)$$

For small forces, the (primed) perturbation terms will be proportional to the force. The asymmetric addition to the potential is connected with f'_{ji} by the Poisson equation:

$$\Delta\psi'_j = -\frac{4\pi}{D} \sum_i \frac{f'_{ji}e_i}{n_j} \quad (2.5.3)$$

The perturbing force sets up an irreversible process in the solution, and the distribution naturally is no longer given by the Boltzmann equation. Hence the general condition (2.2.4) must apply, since \mathbf{v}_j no longer averages to zero. In accordance with the approximation principle of §2.4, we shall assume that the asymmetric addition to the field of a given ion is *proportional to the charge* of the ion, and that we may compute the field due to two ions by linear superposition of the separate fields. For the total force \mathbf{K}_j , acting on an i -ion in the vicinity of a j -ion, we then have

$$\mathbf{K}_{ji} = \mathbf{k}_i - e_i \text{grad}_2 \psi_i(\mathbf{o}) - e_i \text{grad}_2 \psi_j(\mathbf{r}_1, \mathbf{r}_{21}), \quad (2.5.4)$$

where \mathbf{k}_i is the applied external force, $-e_i \text{grad}_2 \psi_i(\mathbf{o})$ is the force due to the ion's own atmosphere and $-e_i \text{grad}_2 \psi_j$ is the force due to the j -ion and the latter's atmosphere. If we substitute (2.5.4) in (2.3.1), we obtain for the first term

$$\begin{aligned} \text{div}_2(f_{ji}\mathbf{v}_{ji}) &= \text{div}_2(f_{ji}\mathbf{V}(\mathbf{r}_2) + \omega_i(f_{ji}\mathbf{k}_i - e_i f_{ji} \text{grad}_2 \psi_i(\mathbf{o}) \\ &\quad - e_i f_{ji} \text{grad}_2 \psi_j(\mathbf{r}_1, \mathbf{r}_{21}) - kT \text{grad}_2 f_{ji})). \end{aligned} \quad (2.5.5)$$

In order to expand this, we note that $\mathbf{V}(\mathbf{r}_2)$ and \mathbf{k}_i are divergence-free, and make the following simplifications. We neglect the term $\text{grad}_2 \psi_i(\mathbf{o})$ since (cf. 2.4.10) it is of the order e_i^2 while the other terms are of the order e_i . We replace f_{ji} in the $\text{grad}_2 \psi_j$ term by $n_j n_i$ since $f_{ji} - n_j n_i \sim e_i$ and the term already has a coefficient e_i .

We thus obtain

$$\begin{aligned} \text{div}_2(f_{ji}\mathbf{v}_{ji}) &= (\mathbf{V}(\mathbf{r}_2), \text{grad}_2 f_{ji}) + \omega_i(\mathbf{k}_i, \text{grad}_2 f_{ji}) \\ &\quad - e_i \omega_i n_i n_j \Delta_2 \psi_j - \omega_i kT \Delta_2 f_{ji} \end{aligned} \quad (2.5.6)$$

We now substitute (2.5.1) and (2.5.2) and note that for $\mathbf{k}_i = \mathbf{o}$, $\mathbf{v}_{ji} = \mathbf{o}$; hence the terms in f° and ψ° must cancel one another except in the two scalar product terms which vanish by hypothesis. We approximate f in these terms by f° . We thus obtain the equation of continuity (2.2.3) specialized to suit our particular problems in the form

$$\begin{aligned} &(\mathbf{V}(\mathbf{r}_2), \text{grad}_2 f^\circ_{ji}) + (\mathbf{V}(\mathbf{r}_1), \text{grad}_1 f^\circ_{ij}) + \\ &\quad \omega_i(\mathbf{k}_i, \text{grad}_2 f^\circ_{ji}) + \omega_j(\mathbf{k}_j, \text{grad}_1 f^\circ_{ij}) - e_i \omega_i n_i n_j \Delta_2 \psi'_j \\ &\quad - e_j \omega_j n_i n_j \Delta_1 \psi'_i - \omega_i kT \Delta_2 f'_{ji} - \omega_j kT \Delta_1 f'_{ij} = 0. \end{aligned} \quad (2.5.7)$$

The first four terms of this equation contain the perturbing factors \mathbf{V} and \mathbf{k} ; the last four represent the asymmetric contributions to potential and dis-

tribution thereby produced. This gives us a system of s^2 differential equations connecting the s^2 distribution functions f'_{ji} with the s potentials ψ_j and the known function $f^0(r)$. Our general procedure in subsequent derivations will be to specialize (2.5.7) to a particular problem, eliminate the f'_{ji} 's by means of the Poisson equation (2.5.3) and solve the resulting system of differential equations for the s potentials ψ'_j .

3. Viscosity

3.1. Description of Problem and Method.

In this section, we shall consider a solution containing s species of ions and shall derive a relation giving the viscosity in terms of the various concentrations.

In order to define clearly the physical conditions of the problem, we shall review briefly the theory of motion in a viscous fluid, bearing in mind the fact that the fluid in question is an electrolytic solution, and shall first show qualitatively how the electrostatic forces between the ions will add to the forces transferred in such motion and estimate their order of magnitude. We picture the solution (see Fig. 2) confined between two parallel plates, h centimeters apart, of which the lower is fixed and the upper moves with constant velocity v' in the x direction, and shall assume for the moment a constant velocity gradient

$$\frac{\partial v_x}{\partial y} = \frac{v'}{h}.$$

in the y direction, so that the velocity at the level y will be

$$v_x = (v'/h)y; v_y = 0, v_z = 0.$$

Recalling the definition of coefficient of viscosity η as the stress transferred per unit velocity gradient, a stress equal to

$$S_{xy} = \eta \frac{\partial v_x}{\partial y}$$

per unit area will be transferred from each layer of liquid to the layer beneath it. In the case of an electrolyte, we shall show that a part of this stress is due to electrostatic forces between the ions. In an undisturbed electrolyte, an ion of charge $+e$ will be surrounded by an atmosphere of total charge $-e$, situated at an average distance $(1/\kappa)$ in which the average distribution is spherically symmetrical since the ions have no preferred orientation. A velocity gradient in the liquid will deform a sphere into an ellipsoid, and the ionic atmospheres will be deformed accordingly. The electrostatic forces and the thermal motion, whose equilibrium determine the structure of the ionic atmospheres, will tend to restore the original structure, but this process of relaxation will not be instantaneous. If the relative rate of deformation is

$$\frac{\partial v_x}{\partial y}$$

and the time of relaxation is τ , a stationary deformation $\tau \frac{\partial v_x}{\partial y}$ will persist. In (1.3.4), it was shown that $\tau = \rho/(\kappa^2 kT)$. The deformation of the ionic atmosphere will then be of the order

$$\frac{\rho}{\kappa^2 kT} \frac{\partial v_x}{\partial y}. \quad (3.1.1)$$

Two ions of charge e , situated at a distance $(1/\kappa)$ exert a Coulomb force on each other equal to $e^2 \kappa^2 / D$ where D is the dielectric constant, so that the total

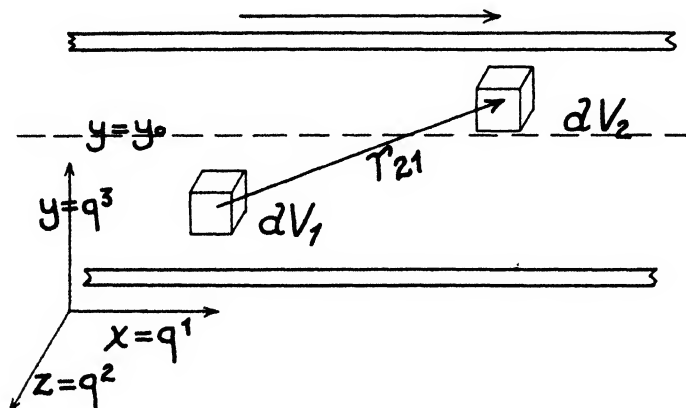


FIG. 2
Sketch for Viscosity Calculation

transport of force (stress) between an ion and its atmosphere without regard to direction is $(1/\kappa) \cdot (e^2 \kappa^2 / D) = e^2 \kappa / D$.

As long as the spherical symmetry of the ionic atmosphere is not disturbed, the stresses in different directions will compensate each other. A velocity gradient in the solution will cause a deformation of the order (3.1.1) as shown above, and we may expect that the resultant directed fraction of the total stress will be of the same order of magnitude. On this basis, the stress transferred between one ion and its atmosphere should be of the order

$$\frac{e^2 \kappa}{D} \frac{\rho}{\kappa^2 kT} \frac{\partial v_x}{\partial y} = \frac{e^2 \rho}{\kappa D kT} \frac{\partial v_x}{\partial y}$$

and that transferred by the interaction of $2n$ ions and their atmospheres of the order

$$\frac{n e^2 \rho}{\kappa D kT} \frac{\partial v_x}{\partial y}$$

or, substituting (2.4.9) for κ^2 and allowing a numerical factor 8π ,

$$S_{yx}^* \approx \kappa \rho \frac{\partial v_x}{\partial y}. \quad (3.1.2)$$

This result is expected to be correct except for a proportionality factor which must be evaluated by considering the exact type of deformation of the ionic atmospheres. Indeed, our final calculations yield for the case of s species of ions, where $\omega_1 = \omega_2 = \dots = \omega_s = \omega = 1/\rho$, the stress

$$S_{xy}^* = \frac{1}{480\pi} \rho \kappa \frac{\partial v_x}{\partial y}. \quad (3.1.3)$$

This stress will be added to the stress transferred by friction between the solvent molecules, namely

$$S_{xy}^0 = \eta_0 \frac{\partial v_x}{\partial y}.$$

Consequently, the electrostatic forces cause an addition

$$\eta^* = \frac{1}{480\pi} \kappa \rho$$

to the viscosity η_0 of the pure solvent. The result of the above consideration is identical with that obtained by Falkenhagen.¹ The essential feature in (3.1.3) is the factor κ ; on account of this factor the electrostatic contribution to viscosity varies as the square root of the concentration of ions. For example, for KCl at 25°C. in water,

$$\eta^* = 44.7 \times 10^{-6} \sqrt{c} = 5.0 \times 10^{-3} \eta_0 \sqrt{c}.$$

For 0.1 n KCl, the electrostatic increase of viscosity amounts to 0.14% of η_0 .

The electrostatic forces between ions will be transferred to the solvent by friction, whereby there must be a relative motion between ions and solvent. This relative motion may take place (in part) in the interior of the solution; however, as we shall show immediately, in certain cases, a relative motion of ions and solvent will take place only along the boundary, namely when the velocity gradient is constant throughout the interior.

If we now consider the general motion in a liquid where the velocity \mathbf{v} at a point located by the vector \mathbf{r} has components v_x, v_y, v_z , the y component of stress per unit area across a plane perpendicular to the x direction is

$$S_{xy} = \eta \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) = S_{yx}. \quad (3.1.4)$$

For a solution of electrolytes, two factors will contribute to the force transfer: first, the friction of solvent on solvent, and second, the interaction of the electrostatic forces between the ions. It is the latter which we wish to investigate. The equations of motion of an incompressible fluid are

$$\eta \Delta \mathbf{v} = \text{grad } p - \mathbf{F} \quad (3.1.5a)$$

$$\text{div } \mathbf{v} = 0, \quad (3.1.5b)$$

¹ Falkenhagen: *Loc. cit.*

where p is the pressure and \mathbf{F} the force per unit volume. If S_{mn}° is the general element of the stress matrix for motion in the pure solvent, then

$$S_{mn} - S_{mn}^\circ = S_{mn}^*$$

represents the average superposed stress due to ionic forces, and correspondingly

$$\eta - \eta^\circ = \eta^* \quad (3.1.6)$$

gives the increase in viscosity of the solution over that of the solvent. On introducing this into the equation of motion, there results

$$\eta^\circ \Delta \mathbf{v} = \text{grad } p - (\mathbf{F} + \eta^* \Delta \mathbf{v}),$$

so that the effect of interionic forces may be interpreted as an addition to the volume force. Furthermore it is evident that wherever $\Delta \mathbf{v}$ vanishes in an interior region of the liquid, no force will be transferred from the ions to the solvent in that region. In the case of a constant velocity gradient, as in our example above, $\Delta \mathbf{v} = 0$ everywhere in the liquid. Still, the forces acting on the plates A and B (per unit area) equal $(\pm)\eta \partial v_x / \partial y$ and not $\eta^\circ \partial v_x / \partial y$. The difference $\eta^* \partial v_x / \partial y$ can be accounted for if we assume that the ions move relatively to the solvent along the boundaries (up to distances $1/\kappa$) and nowhere else, with a velocity that is sufficient to produce the required frictional force.

The flow of ions along a boundary is not easily calculated by direct methods although our consideration above shows that such an effect must be present. However, we shall calculate directly the relative motion of ions and solvent in the interior of the solution, that is, when $\Delta \mathbf{v} \neq 0$, and we shall show that the forces derivable from the potentials of the asymmetric "odd" ionic fields agree with the term $\eta^* \Delta \mathbf{v}$ calculated from the stress S_{mn}^* . The contribution S_{mn}^* to the stress due to the presence of ions will be computed by the following method: By means of the Poisson equation (2.5.3) and the equation of continuity (2.5.7), we shall derive a system of differential equations which determine the potentials of the ionic fields, and give their solution for the general case of a mixture of s species of ions. Then S_{mn}^* will be computed as the average sum of the corresponding components of the electrical forces between all pairs of ions present, which will require the distribution function $f_{ji}(\mathbf{r}_{21}) = f_{ij}(\mathbf{r}_{12})$, giving the average concentration of i -ions in the vicinity of a j -ion and vice versa. By means of the Poisson equation, however, $f_{ji}(\mathbf{r}_{21})$ may be replaced by the potentials which have been obtained by solving the differential equations, and we shall have in explicit form the result desired.

3.2. Evaluation of Velocity Terms in the Equation of Continuity.

In accordance with the considerations of the previous paragraph regarding the nature of the velocity field, we shall expand the velocity as a Taylor series in the coordinates and neglect terms of higher order than the second, so

¹ In the case of a constant velocity gradient, the potential in the ionic atmosphere is an even function of the distance in the sense that $\psi(x, y, z) = \psi(-x, -y, -z)$. A variable gradient will cause "odd" contributions to the field of the atmosphere.

that the velocity gradient will, to this approximation, be a linear function of the variables $q^1 = x$, $q^2 = y$, $q^3 = z$. We then have for the general component of the velocity at a point located by the vector \mathbf{r}

$$v^l(\mathbf{r}) = v^l(\mathbf{o}) + \sum_{\lambda=1}^3 q^\lambda \left(\frac{\partial v^l}{\partial q^\lambda} \right)_{\mathbf{r}=\mathbf{o}} + \frac{1}{2} \sum_{\lambda=1}^3 \sum_{\mu=1}^3 q^\lambda q^\mu \left(\frac{\partial^2 v^l}{\partial q^\lambda \partial q^\mu} \right)_{\mathbf{r}=\mathbf{o}}.$$

For convenience, we shall use the convention that Greek indices always imply summation, and introduce the following abbreviations:

$$a_m^l = \left(\frac{\partial v^l}{\partial q^m} \right)_{\mathbf{r}=\mathbf{o}},$$

$$b_{mn}^l = \left(\frac{\partial^2 v^l}{\partial q^m \partial q^n} \right)_{\mathbf{r}=\mathbf{o}} = b_{nm}^l,$$

so that our expansion may be written compactly as

$$v^l(\mathbf{r}) = v^l(\mathbf{o}) + a_\lambda^l q^\lambda + \frac{1}{2} b_{\lambda\mu}^l q^\lambda q^\mu. \quad (3.2.1)$$

For dealing with the motion in an ionic atmosphere, we shall find it convenient to shift the origin to a point \mathbf{r}_1 , (specifying the position of the central ion). The velocity at another point \mathbf{r}_2 (where another ion might be found) will be

$$v^l(\mathbf{r}_2) = v^l(\mathbf{r}_1) + q^\lambda{}_{21} c_\lambda^l(\mathbf{r}_1) + \frac{1}{2} q^\mu{}_{21} q^\nu{}_{21} b_{\mu\nu}^l, \quad (3.2.2)$$

where $q^l{}_{21} = x_2 - x_1$, etc.

We identify the c_m^l 's by substitution of (3.2.1) for $v^l(\mathbf{r}_2)$ and $v^l(\mathbf{r}_1)$ into (3.2.2) and comparison of coefficients to be

$$c_m^l(\mathbf{r}_1) = a_m^l + b_{m\sigma}^l q^\sigma{}_{11}. \quad (3.2.2b)$$

The coefficients have the following properties by their definition:

$$a_\mu^\nu = a_\mu^\nu, \quad c_\nu^\mu = c_\nu^\mu, \quad (3.2.3)$$

and the requirement that the solution be incompressible (3.1.5b)

$$0 = \text{div } \mathbf{v} = a_\mu^\mu + \frac{1}{2} b_{\mu\nu}^\mu q^\nu + \frac{1}{2} b_{\nu\mu}^\mu q^\mu = c_\mu^\mu$$

gives the additional properties that

$$a_\mu^\mu = 0; \quad b_{\mu\nu}^\mu = b_{\nu\mu}^\mu = 0; \quad c_\mu^\mu = 0. \quad (3.2.4)$$

The velocity terms in the equation of continuity may now be evaluated. Since by definition (2.1.6) $f_{ji}^\circ(r) = f_{ij}^\circ(r)$ and $q_{21} = q_2 - q_1$, we have

$$\text{grad}_2^l f_{ji}^\circ(r) = \left(\frac{\partial}{\partial q_2^l} f_{ji}^\circ(r) \right)_{r_1 = \text{const}} = \frac{\partial}{\partial q_2^l} f_{ji}^\circ(r) \equiv D_l f_{ji}^\circ(r)$$

$$\text{grad}_1^l f_{ij}^\circ(r) = \left(\frac{\partial}{\partial q_1^l} f_{ij}^\circ(r) \right)_{r_2 = \text{const}} = - \left(\frac{\partial}{\partial q_1^l} f_{ij}^\circ(r) \right) \equiv - D_l f_{ij}^\circ(r)$$

Substitution of these and (3.2.2) in the velocity terms gives

$$((\mathbf{V}(\mathbf{r}_2), \text{grad}_2 f_{ji}^\circ(r)) + (\mathbf{V}(\mathbf{r}_1), \text{grad}_1 f_{ji}^\circ(r))) =$$

$$c_\lambda^\lambda q^\mu D_\lambda f_{ji}^\circ(r) + \frac{1}{2} b_{\lambda\mu}^\lambda q^\mu q^\nu D_\lambda f_{ji}^\circ(r).$$

This polynomial may be written in a more convenient form, (which may be verified by substitution of (3.2.6) and using (3.2.4) and the fact that

$$D_i f(r) = q^i \left(\frac{df(r)}{r dr} \right), \text{ as follows} \quad (3.2.5)$$

$$c_{\mu}^{\lambda} D_{\lambda\mu}^2 \zeta(r) + \frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 \theta(r) - \frac{1}{2} b_{\lambda\mu\mu} D_{\lambda} \zeta(r)$$

when the functions $\zeta(r)$ and $\theta(r)$ are defined by

$$f_{\circ j}(r) = \frac{d\zeta(r)}{r dr} = \frac{d^2\theta(r)}{(r dr)^2}. \quad (3.2.6)$$

This device, which will be employed consistently in the following, serves to convert a rather unwieldy polynomial into a sum of derivatives of functions of r alone. In this form, we may consider the various quantities to be functions of r with operator coefficients, which commute agreeably with other partial differentiation operators, such as $\Delta = D_{\lambda\lambda}^2$.

3.3. Transformation of Vector Variables.

When we recall that the derivation of the equation of continuity involved two terms, one of which referred to the volume element dV_1 and the other to dV_2 , it is clear that the final form (2.5.7) will include functions of both \mathbf{r}_1 and \mathbf{r}_2 , as well as \mathbf{r}_{21} and \mathbf{r}_{12} as independent variables. With the help of the relations

$$\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}_{21} = -\mathbf{r}_{12},$$

we shall transform the terms to functions of \mathbf{r}_1 and \mathbf{r}_{21} as independent variables. We have to deal with functions of the type $\varphi(\mathbf{r}_1, \mathbf{r}_{21})$ (or equally well $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$), describing the conditions in the atmosphere of an ion situated at $\mathbf{r}_1(\mathbf{r}_2)$ at the distance $\mathbf{r}_{21}(\mathbf{r}_{12})$ from this ion. The asymmetry of the ionic atmospheres will be proportional to the velocity gradient. We have assumed that the latter varies linearly with location, and we may make the same assumption for the function φ , namely that $\varphi(\mathbf{r}_1, \mathbf{r}_{21})$ is linear in \mathbf{r}_1 .

Our task is to express a function $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$, (linear in \mathbf{r}_2) in the variables $\mathbf{r}_1, \mathbf{r}_{21}$. We introduce an operator "Grad" defined by

$$\text{Grad}^i \varphi = \left\{ \left(\frac{\partial}{\partial q_1^i} \right)_{\mathbf{r}_2} + \left(\frac{\partial}{\partial q_2^i} \right)_{\mathbf{r}_1} \right\} \varphi \quad (3.3.1)$$

which refers to displacement of an ion together with its atmosphere. The transformation of $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$ then becomes

$$\varphi(\mathbf{r}_2, \mathbf{r}_{12}) = \varphi, (\mathbf{r}_1 - \mathbf{r}_{21}) + (\mathbf{r}_{21}, \text{Grad } \varphi(\mathbf{r}_1, -\mathbf{r}_{21})). \quad (3.3.2)$$

Obviously

$$\text{Grad}^i \varphi(\mathbf{r}_1, \mathbf{r}_{21}) = \left(\frac{\partial}{\partial q_1^i} \varphi(\mathbf{r}_1, \mathbf{r}_{21}) \right)_{\mathbf{r}_{21} = \text{const.}}$$

Using (3.3.2) and the fact that

$$\Delta_1 \varphi(\mathbf{r}_2, \mathbf{r}_{12}) = \left(\frac{\partial^2 \varphi}{\partial q_{\lambda_1}^2 \partial q_{\lambda_1}^2} \right)_{\mathbf{r}_2} = \left(\frac{\partial^2 \varphi}{\partial q_{\lambda_{21}}^2 \partial q_{\lambda_{21}}^2} \right) = \Delta \varphi,$$

we obtain

$$\Delta_1 \psi'_i(\mathbf{r}_2, \mathbf{r}_{12}) = \Delta \psi'_i(\mathbf{r}_1, -\mathbf{r}_{21}) + (\mathbf{r}_{21}, \text{Grad } \Delta \psi'_i(\mathbf{r}_1, -\mathbf{r}_{21})). \quad (3.3.3)$$

From the symmetry condition (2.1.6)

$$\Delta_1 f'_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = \Delta_1 f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$$

and the identity

$$\Delta_1 \equiv \frac{\partial^2}{\partial q^{\lambda_1} \partial q^{\lambda_1}} \equiv \left(\text{Grad}^{\lambda} - \frac{\partial}{\partial q^{\lambda_2}} \right)^2,$$

we find that

$$\begin{aligned} \Delta_1 f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) &= \Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) + \text{Div Grad } f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) - 2 \frac{\partial^2}{\partial q^{\lambda_{21}} \partial q^{\lambda_1}} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \\ &= \Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) - 2 \frac{\partial^2}{\partial q^{\lambda_{21}} \partial q^{\lambda_1}} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}). \end{aligned} \quad (3.3.4)$$

(we recall that f'_{ji} is a linear function of \mathbf{r}_1 , annihilated by the operator Div Grad).

3.4 The Differential Equations for the Potentials.

If now (3.2.5), (3.3.3) and (3.3.4) are substituted in the equation of continuity (2.5.7), and the external forces \mathbf{K}_i and \mathbf{K}_j are set equal to zero, we obtain the system of s^2 differential equations

$$\begin{aligned} (c_{\mu}^{\lambda} D_{\lambda\mu}^2 \zeta(r) + \frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 \theta(r) - \frac{1}{2} b_{\mu\mu}^{\lambda} D_{\lambda} \zeta(r)) - e_i \omega_i n_i n_j \Delta \psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) \\ - e_j \omega_j n_i n_j \Delta \psi'_i(\mathbf{r}_1, -\mathbf{r}_{21}) - (\omega_i + \omega_j) k T \Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \\ - e_j \omega_j n_i n_j(\mathbf{r}_{21}, \Delta \text{Grad } \psi'_i) + 2 \omega_j k T \frac{\partial^2}{\partial q^{\lambda_{21}} \partial q^{\lambda_1}} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = 0 \end{aligned} \quad (3.4.1)$$

which connect the s^2 distribution functions f'_{ji} with the s potentials ψ'_j for the case that a velocity gradient described by (3.2.1) is present in an electrolyte, while there are no external forces acting on the ions. The system (3.4.1) is made complete by means of the s Poisson equations (2.5.3).

The functions ψ'_j and f'_{ji} which give the deviations of potential and distribution from their values ψ_j^0 and f_{ji}^0 characteristic of the solution at rest, depend on distance and direction between pairs of ions and hence may be expanded in the form

$$\sum_n A_n q^{\lambda} \dots q^{\mu} g_n(r),$$

or preferably in the more convenient form (compare with 3.2.5)

$$\sum_n B_n D_{\lambda}^n \dots \mu h_n(r).$$

The original assumption of a linear velocity gradient leads to three types of terms in the known function of r (3.2.5) which appears in (3.4.1) and therefore to the same approximation, we may set

$$\begin{aligned} \psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) &= b_{\mu\mu}^{\lambda} D_{\lambda} v_j(r) + c_{\nu}^{\mu} D_{\mu\nu}^2 \xi_j(r) + \frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 u_j(r) \\ f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) &= b_{\mu\mu}^{\lambda} D_{\lambda} G_{ji}(r) + c_{\nu}^{\mu} D_{\mu\nu}^2 \varphi_{ji}(r) + \frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 F_{ji}(r) \\ \psi'_i(\mathbf{r}_1, -\mathbf{r}_{21}) &= -b_{\mu\mu}^{\lambda} D_{\lambda} v_i(r) + c_{\nu}^{\mu} D_{\mu\nu}^2 \xi_i(r) - \frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 u_i(r). \end{aligned} \quad (3.4.2)$$

(In $\psi'_i(\mathbf{r}_1, -\mathbf{r}_{21})$, the odd terms obtain the sign minus because the differentiations indicated by D are with respect to the components of $+\mathbf{r}_{21}$). Substitution of (3.4.2) in (3.4.1) gives an equation of the form

$$b_{\mu\mu}^{\lambda} D_{\lambda} L_1 \{U_1(r)\} + c_{\nu}^{\mu} D_{\mu\nu}^2 L_2 \{U_2(r)\} + b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 L_3 \{U_3(r)\} = 0 \quad (3.4.3)$$

(since the order of partial differentiation is immaterial), where the L 's represent symbolically the three parts of the resulting equation. This is equivalent to three equations

$$b_{\mu\mu}^{\lambda} D_{\lambda} L_1 \{U_1(r)\} = 0 \quad (3.4.4)$$

$$c_{\mu}^{\lambda} D_{\mu\nu}^2 L_2 \{U_2(r)\} = 0 \quad (3.4.5)$$

$$b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^3 L_3 \{U_3(r)\} = 0, \quad (3.4.6)$$

for (3.4.3), a polynomial in the coordinates, can vanish only if the coefficients vanish separately.

Now the stress S_{im}^* is to be computed as an average sum of the forces between ions and it will be seen that the averaging process will eliminate terms of the sum involving odd powers of the coordinates. Consequently we shall need to compute only the even part $c_{\nu}^{\mu} D_{\mu\nu}^2 \xi(r)$ of the potential in order to evaluate the stress and shall require the odd terms only for the special consideration of the mechanism of force transfer. (Appendix II). Our immediate problem then is the solution of

$$c_{\nu}^{\mu} D_{\mu\nu}^2 L_2 \{U_2(r)\} = 0.$$

Since $L_2 \{U_2(r)\}$ is a function $R(r)$ of r , this is equivalent to

$$c_{\nu}^{\mu} D_{\mu\nu}^2 q^{\mu} q^{\nu} \frac{d^2 R(r)}{(r dr)^2} = 0,$$

(because by (3.2.4), $c_{\mu}^{\mu} = c_{\nu}^{\nu} = 0$), and has the solution

$$R(r) = A_1 r^2 + A_2, \quad (3.4.7)$$

where A_1 and A_2 are constants to be determined by the boundary condition that the potential must vanish for r large. We substitute (3.4.3) in (3.4.1), select the even terms, and obtain

$$c_{\nu}^{\mu} D_{\mu\nu}^2 \{\xi(r) - e_i \omega_i n_i n_j \Delta \xi_j - e_j \omega_j n_i n_j \Delta \xi_i - (\omega_i + \omega_j) kT \Delta \varphi_{ji}\} = 0 \quad (3.4.8)$$

(the last two terms of (3.4.1) contain only odd functions of the coordinates).

The distribution function $\Delta \varphi_{ji}$ is eliminated from (3.4.8) by means of the relation

$$c_{\nu}^{\mu} D_{\mu\nu}^2 \left(\Delta \xi_j + \frac{4\pi}{D} \sum_i \frac{e_i}{n_j} \varphi_{ji} \right) = 0 \quad (3.4.9)$$

obtained by substituting (3.4.2) in the Poisson equation and selecting the even part. This elimination gives us s equations to determine the even part of the s potentials $\psi'_{,j}$, namely $c_{\nu}^{\mu} D_{\mu\nu}^2 \xi_j(r)$, as follows:

$$\begin{aligned} c_{\nu}^{\mu} D_{\mu}^2 \cdot \left(\Delta \Delta \xi_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta \xi_j - \frac{4\pi}{DkT} \sum_i \frac{e_i e_j \omega_j n_i}{\omega_i + \omega_j} \Delta \xi_i \right. \\ \left. + \frac{4\pi}{DkT} \sum_i \frac{e_i}{n_j} \frac{\xi(r)}{\omega_i + \omega_j} \right) = 0. \end{aligned} \quad (3.4.10)$$

Recalling the definition (3.2.6) of $\zeta(r)$

$$\frac{d\zeta(r)}{r dr} = n_j n_i \left(1 - \frac{e_j e_i}{DkT} \frac{e^{-\kappa r}}{r} \right),$$

$\zeta(r)$ is found by integration to be

$$\zeta(r) = \frac{e_j e_i n_j n_i}{\kappa DkT} e^{-\kappa r} + \frac{n_j n_i}{2} r^2 + C_1.$$

This is substituted in (3.4.10), the integration (3.4.7) is performed and the constants A_1 and A_2 are chosen to eliminate the last two terms of $\zeta(r)$, as required by the boundary conditions. Thus we obtain in the final form the equations which determine $\xi_j(r)$:

$$\begin{aligned} \Delta \Delta \xi_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta \xi_j - \frac{4\pi}{DkT} \sum_i \frac{e_i e_j \omega_j n_i}{\omega_i + \omega_j} \Delta \xi_i \\ = - \frac{4\pi}{(DkT)^2} \frac{e^{-\kappa r}}{\kappa} \sum_i \frac{n_i e_i^2 e_j}{\omega_i + \omega_j}. \end{aligned} \quad (3.4.11)$$

3.5. Matrix Formation and Solution.

The s equations (3.4.11) which determine the even parts of the potentials ψ'_j of the distorted ionic atmospheres can be dealt with most conveniently with the aid of the theory of quadratic forms. We shall first write (3.4.11) in a more compact form by the use of the following notation:

$$a_{ji} = \left(\delta_{ji} \sum_{k=1}^s \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \right) \frac{4\pi}{DkT} \quad (3.5.1)$$

$$t_j = \frac{-4\pi}{(DkT)^2 \kappa} \sum_{i=1}^s \frac{n_i e_i^2}{\omega_i + \omega_j} e_j, \quad (3.5.2)$$

where δ_{ji} is the well known Kronecker symbol

$$\delta_{ji} = \begin{cases} 1, & \text{if } j = i \\ 0, & \text{if } j \neq i. \end{cases}$$

In this notation, (3.4.11) becomes

$$\sum_{i=1}^s \Delta(\Delta \delta_{ji} - a_{ji}) \xi_i = t_j e^{-\kappa r} \quad (3.5.3)$$

or, using the convention that Greek indices imply summation (here, of course, from 1 to s),

$$\Delta(\Delta \delta_{j\sigma} - a_{j\sigma}) \xi_\sigma = t_j e^{-\kappa r}. \quad (3.5.4)$$

If we now introduce a space of s dimensions, t_j may be considered as the j -th component of a vector \mathbf{t} in this space, and a_{ji} as the i -th element of the j -th row of a matrix A or the corresponding element of the tensor operator \mathbf{A} . Also δ_{ji} is the general component of the unit matrix E

$$E = \begin{pmatrix} 1 & 0 & . & . & . & 0 \\ 0 & 1 & . & . & . & 0 \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & 1 \end{pmatrix} = (\delta_{ji})$$

corresponding to the unit tensor $\mathbf{E} = 1$.

Then (3.5.4) may be interpreted as a linear operation

$$\Delta(\Delta - \mathbf{A}) \mathbf{x} = \mathbf{t} e^{-\kappa r} \quad (3.5.5)$$

where $\Delta(\Delta - \mathbf{A})$ acting on an unknown vector \mathbf{x} (which is a function of r) produces a known vector \mathbf{t} multiplied by the known scalar function $\exp(-\kappa r)$.

We shall show later in discussing the matrix \mathbf{A} , that its "characteristic numbers" $\alpha_1, \alpha_2, \dots, \alpha_s$ are all positive. That being the case, it is possible to find matrices \mathbf{B} , such that

$$\mathbf{B}^2 = \mathbf{A} : b_{j\lambda} b_{\lambda i} = a_{ji} \quad (3.5.6)$$

and a matrix \mathbf{B} with this property will be real. The equation (3.5.6) has actually several (in general 2^s) solutions \mathbf{B} , with the characteristic numbers $\pm\sqrt{\alpha_1}, \dots, \pm\sqrt{\alpha_s}$. Among these solutions we shall select the one that has only positive characteristic numbers $+\sqrt{\alpha_1}, \dots, +\sqrt{\alpha_s}$, and designate it simply as \mathbf{B} .

Now if $\chi(r, \beta)$ is the solution of

$$\Delta(\Delta - \beta^2) \chi(r, \beta) = e^{-\kappa r} \quad (3.5.7a)$$

then¹

$$\Delta(\Delta - \mathbf{B}^2) \chi(r, \mathbf{B}) = e^{-\kappa r} \mathbf{1}, \quad (3.5.7b)$$

so that $\Delta(\Delta - \mathbf{B}^2) \chi(r, \mathbf{B})$ operating on \mathbf{t} is equivalent to multiplying \mathbf{t} by the scalar $e^{-\kappa r}$; that is,

$$\mathbf{x} = \chi(r, \mathbf{B}) \mathbf{t} \quad (3.5.8)$$

is the solution of (3.5.5). We therefore investigate the solution of (3.5.7a).

A particular solution is

$$\chi(r, \beta) = \frac{\partial}{\partial \kappa} \left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)} \frac{e^{-\kappa r}}{r} \right),$$

to which must be added the general solution of the homogeneous equation, giving as the complete solution

$$\chi(r, \beta) = \frac{\partial}{\partial \kappa} \left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)} \frac{e^{-\kappa r}}{r} \right) + A_1 \frac{e^{-\beta r}}{r} + A_2 \frac{1}{r} + A_3 \frac{e^{\beta r}}{r} + A_4 r^2. \quad (3.5.9)$$

¹ A polynomial function $P(\mathbf{B})$ is defined as

$$\sum_{\nu=1}^n a_\nu \mathbf{B}^\nu \quad \text{if } P(\beta) = \sum_{\nu=1}^n a_\nu \beta^\nu.$$

The reciprocal $(\chi(\mathbf{B}))^{-1}$ of a function $\chi(\mathbf{B})$ is defined by $\chi(\mathbf{B}) (\chi(\mathbf{B}))^{-1} = 1$ (assuming that $\chi(\mathbf{B})$ is not a degenerate matrix, that is, its determinant $|\chi(\mathbf{B})|$ must not vanish.) An n -th root $\mathbf{A}^{1/n}$, which is, of course, multiple-valued, is defined by $(\mathbf{A}^{1/n})^n = \mathbf{A}$. A transcendental function may be defined by its power series if it converges, which is certainly the case for an entire function, e.g. the exponential function. This list includes all the functions of matrices that we shall need.

The constants $A_1 \dots A_4$ must be evaluated by the boundary conditions of our problem. Let us assume for a moment, in analogy with (3.4.2), that

$$c^\lambda_\mu D^2_{\lambda\mu}\chi(r, \beta) \equiv O_2\{\chi(r, \beta)\} = c^1_1 \frac{\partial^2 \chi}{\partial x^2} + 2 c^1_2 \frac{\partial^2 \chi}{\partial x \partial y} + \dots + c^3_3 \frac{\partial^2 \chi}{\partial z^2}$$

where $c^\lambda_\lambda = c^1_1 + c^2_2 + c^3_3$ (cf. (3.2.4)), describes the potential in the neighborhood of an ion (except for a constant factor, corresponding to t in (3.5.5)). Then the following boundary conditions must hold: For $r = \infty$, $O_2\{\chi\}$ must vanish, or the ion would make its presence felt at infinite distance. For $r = 0$, we must require that the power series for $\chi(r)$ and for $\Delta\chi(r)$ contain no negative powers of r : A term ($1/r$) in the expansion of $\chi(r)$ would lead to a singularity $O_2\{1/r\} = c^\lambda_\mu D^2_{\lambda\mu}(1/r)$ in the potential $O_2(\chi)$. According to potential theory such a singularity represents a quadrupole at $r = 0$, which is inadmissible. A term ($1/r$) in $\Delta\chi$ must be excluded because $\Delta(O_2\{\chi\}) = O_2\{\Delta\chi\}$ is proportional to the charge density and

$$O_2\{1/r\} = c^\lambda_\mu q^\mu q^\nu \frac{1}{r^5}$$

is not even integrable near $r = 0$, and would imply an infinite charge present in a finite volume.

The boundary condition for $r = \infty$ then requires

$$A_3 = A_4 = 0.$$

The power series for $\chi(r, \beta)$ starts with the term

$$\left(\frac{\partial}{\partial \kappa} \left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)} \right) + A_1 + A_2 \right) \frac{1}{r}$$

and the series for $\Delta\chi$ with

$$\left(\frac{\partial}{\partial \kappa} \left(\frac{1}{\beta^2 - \kappa^2} \right) + A_1 \beta^2 \right) \frac{1}{r}$$

and there are no other negative powers of r to be considered. The necessary and sufficient requirements for fulfilling our boundary conditions are therefore:

$$A_1 = \frac{\partial}{\partial \kappa} \left(\frac{-1}{\beta^2(\beta^2 - \kappa^2)} \right)$$

$$A_2 = \frac{\partial}{\partial \kappa} \left(\frac{-1}{\beta^2 \kappa^2} \right).$$

Inserting these values in (3.5.9) we obtain

$$\chi(r, \beta) = \frac{\partial}{\partial \kappa} \left(\frac{\beta^2 e^{-\kappa r} - \kappa^2 e^{-\beta r} - (\beta^2 - \kappa^2)}{\beta^2 \kappa^2 (\beta^2 - \kappa^2) r} \right). \quad (3.5.10)$$

This solution holds for all positive values of β . In order to cover the special case $\beta = \kappa$, we need only point out that the factor $(\beta - \kappa)$ in the denominator is really harmless, because it can be divided out from the expanded power series of the numerator.

Now consider

$$\chi(r, \mathbf{B}) = \frac{1}{r} \frac{\partial}{\partial \kappa} (\kappa^{-2} (\mathbf{B}^2 - \kappa^2)^{-1} e^{-\kappa r} - \mathbf{B}^{-2} (\mathbf{B}^2 - \kappa^2)^{-1} \exp(-\mathbf{B}r) - \kappa^{-2} \mathbf{B}^{-2})$$

which, since the presence of only one matrix or functions thereof does not affect the rules of algebra¹ will be a (particular) solution of (3.5.7b), as (3.5.10) is a solution of (3.5.7a). Furthermore,

$$\mathbf{x}(r) = \chi(r, \mathbf{B}) \mathbf{t}$$

is a particular solution of (3.5.5).

Since we have already adjusted the arbitrary constants in $\chi(r, \beta)$ to satisfy the boundary conditions for a potential, we may expect that the components ξ_1, \dots, ξ_n of \mathbf{x} , (or rather $c^\lambda_\mu D_{\lambda\mu} \xi_i$, etc.) will be equally agreeable. Indeed, we have chosen all the characteristic values of B positive, so that $\exp(-\mathbf{B}r)$ will vanish for $r = \infty$ and the same applies to all components of $(\exp(-\mathbf{B}r), \mathbf{t})$. It is fairly obvious that the other terms in $\chi(r, \mathbf{B})$ vanish for $r = \infty$. As regards the boundary conditions for $r = 0$, we have shown already that $\chi(r, \beta)$ and $\Delta\chi(r, \beta)$ contain no negative powers of r ; similarly, neither $\chi(r, \mathbf{B})$ nor $\Delta\chi(r, \mathbf{B})$ will contain negative powers of r . The same, then, applies to $\xi_j(r)$ and $\Delta\xi_j(r)$, which are the j -components of

$$\mathbf{x} = (\chi(r, \mathbf{B}), \mathbf{t}) \quad (3.5.11)$$

and

$$\Delta\mathbf{x} = (\Delta\chi(r, \mathbf{B}), \mathbf{t}) \quad (3.5.12)$$

respectively. Thus (3.5.11) is a solution of (3.5.5), satisfying the appropriate boundary conditions. It remains to demonstrate that this solution is unique. For that purpose we consider the most general solution of the homogeneous equation

$$\Delta(\Delta - \mathbf{B}^2) \mathbf{x}^* = 0,$$

which is

$$\mathbf{x}^* = \frac{1}{r} \left(\exp(-\mathbf{B}r), \mathbf{a} \right) + \frac{1}{r} \mathbf{b} + \frac{1}{r} \left(\exp \mathbf{B}r, \mathbf{c} \right) + r^2 \mathbf{d}$$

where \mathbf{a} , \mathbf{b} , \mathbf{c} and \mathbf{d} are arbitrary vectors. If we could find vectors \mathbf{a} , \mathbf{b} , \mathbf{c} , \mathbf{d} (not all zero) such that (every component of) \mathbf{x}^* would satisfy the above boundary conditions (\mathbf{x}^* and $\Delta\mathbf{x}^*$ free from singularities for $r = 0$, $\mathbf{x}^* \rightarrow 0$ for $r \rightarrow \infty$), we might add \mathbf{x}^* to (3.5.11). That, however, is not the case, so that (3.5.11) is unique. Written in components, (3.5.11) takes the form

$$\xi_j(r) = \chi(r, B)_{j\sigma} t_\sigma \quad (3.5.13)$$

It will turn out that we shall need only the value of $\Delta\xi_j$ for $r = 0$ in order to compute the stress S^*_{mn} ; we shall therefore anticipate somewhat by evaluating $\Delta\xi_j(0)$ at this point. By differentiating (3.5.10), we obtain

¹ It takes two matrices to form a non-commutative product.

$$\Delta\chi(r, \beta) = \frac{\partial}{\partial \kappa} \left(\frac{e^{-\kappa r} - e^{-\beta r}}{r(\beta^2 - \kappa^2)} \right) \quad (3.5.14)$$

and

$$\begin{aligned} \Delta\chi(0, \beta) &= \lim_{r \rightarrow 0} \frac{\partial}{\partial \kappa} \left(\frac{(1 - \kappa r + \frac{1}{2} \kappa^2 r^2 + \dots) - (1 - \beta r + \frac{1}{2} \beta^2 r^2 + \dots) + \dots}{r(\beta + \kappa)(\beta - \kappa)} \right) \\ &= \frac{\partial}{\partial \kappa} \left(\frac{1}{\beta + \kappa} \right) = \frac{-1}{(\beta + \kappa)^2}. \end{aligned} \quad (3.5.15)$$

Similarly

$$\Delta\xi_j(0) = -(B + \kappa)^{-2}_{j\sigma} t_\sigma. \quad (3.5.16)$$

3.6. Calculation of Stress.

In accordance with our preliminary consideration in §3.1, we imagine the electrolyte confined between two plates, (Fig. 2), one of which moves in the x -direction, and investigate the total transport of electrostatic force AS^*_{yx} across an area A of a plane $y = y_0$ in the x -direction, assuming a velocity gradient with only one component

$$\frac{\partial v_x}{\partial y} = a^1_2.$$

The Coulomb force between any two ions is

$$\frac{e_j e_i}{D} \frac{\mathbf{r}_{21}}{r^3},$$

where \mathbf{r}_{21} is the vector which locates the second ion with respect to the first. Now if a pair of ions is to contribute anything to AS^*_{yx} , the stress across the plane, they must obviously be on opposite sides of the plane $y = y_0$, so that we must consider only pairs of ions whose coordinates satisfy the restriction

$$y_1 < y_0 < y_2$$

If \mathbf{r}_1 locates the first ion and \mathbf{r}_2 the second. Let us now calculate the mutual forces between the ions in two volume elements dV_1 and dV_2 , located on opposite sides of the plane. The force transferred from a j -ion in dV_1 to the ions in dV_2 is

$$\frac{e_j}{D} \sum_i e_i n_{ji}(\mathbf{r}_{21}) dV_2 \frac{\mathbf{r}_{21}}{r^3}.$$

The total interaction between all pairs of ions in the two volume elements is then:

$$\begin{aligned} \sum_j \frac{n_j e_j}{D} dV_1 \sum_i e_i n_{ji}(\mathbf{r}_{21}) dV_2 \frac{\mathbf{r}_{21}}{r^3} &= \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) dV_1 dV_2 \frac{\mathbf{r}_{21}}{r^3} \\ &= - \sum_{ji} \frac{e_i e_j}{D} f_{ij}(\mathbf{r}_{12}) dV_1 dV_2 \frac{\mathbf{r}_{12}}{r^3}. \end{aligned}$$

The total transfer of force across a plane $y = y_0$ is obtained by integrating over all volume elements satisfying the condition $y_1 < y_0 < y_2$. Thus, if the

area of the plane $y = y_0$ be $A = \int dz dx$, the x component of the force transferred across this plane equals¹

$$\begin{aligned} -AS^*_{yx} &= \iiint_{y_1 < y_0 < y_2} \iiint \sum \frac{e_i e_j}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21}}{r^3} dV_1 dV_2 \\ &= \iiint_{y_{21} > 0} \iiint \sum_j \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21}}{r^3} dx_1 dy_1 dz_1 dV_{21}. \end{aligned} \quad (3.6.1)$$

$$y_0 - y_{21} < y_1 < y_0$$

Integration over x_1 and z_1 yields a factor A ; integration over y_1 a factor y_{21} . Thus

$$-S^*_{yx} = \iiint_{y_{21} > 0} \sum_j \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21} y_{21}}{r^3} dV_{21}$$

or, since we may now drop the indices 21 without causing confusion

$$-S^*_{yx} = \iiint_{+y > 0} \frac{xy}{r^3} \sum_j \frac{e_j e_i}{D} f_{ji}(\mathbf{r}) dV.$$

We may extend the region of integration to the whole space by utilizing the identity $f_{ji}(\mathbf{r}) = f_{ij}(-\mathbf{r})$ whence, interchanging indices of summation

$$\frac{xy}{r^3} \sum_j \frac{e_j e_i}{D} f_{ji}(\mathbf{r}) = \frac{(-x)(-y)}{r^3} \sum_{ij} \frac{e_i e_j}{D} f_{ij}(-\mathbf{r}).$$

Introducing the arithmetic mean of right and left-hand members of this into (3.6.1), we obtain

$$S^*_{yx} = -\frac{1}{2} \int \int_{-\infty}^{+\infty} \int \frac{xy}{r^3} \sum_j \frac{e_j e_i}{D} f_{ji}(\mathbf{r}) dV.$$

By means of the Poisson equation (2.5.3), the potential sum $\sum_j \psi_j$ is substituted:

$$S^*_{yx} = \frac{1}{8\pi} \int \int_{-\infty}^{+\infty} \int \sum_j n_j e_j \Delta \psi_j(\mathbf{r}_{21}) \frac{xy}{r^3} dV.$$

We shall now compute this integral. Since $\psi_j(\mathbf{r}_{21}) = \psi_j^0(r) + \psi'_j(\mathbf{r}_{21})$, the contribution to the integral of the potential $\psi_j^0(r)$ characteristic of the undisturbed state will be nil since $\Delta \psi_j$ is multiplied by xy . Likewise, the terms of ψ'_j which are odd in the coordinates will average out, so that the integral reduces to

$$S^*_{yx} = \frac{1}{8\pi} \int \int_{-\infty}^{+\infty} \int \sum_j n_j e_j (a^\lambda{}_\mu D^2{}_{\lambda\mu} \Delta \xi_j(r)) \frac{xy}{r^3} dV$$

in view of the definition of ξ_j in (3.4.2) and of c_m^l in (3.2.2).

¹ We use the customary sign convention that pressures are reckoned negative and tensions positive. Here we clearly have to do with a pressure: the Coulomb law as written is positive for a repulsive force.

For the special case under consideration, namely, $a^1_2 = a^1_2$, $a^l_m = 0$ otherwise, we obtain

$$\begin{aligned} S^*_{yx} &= \frac{1}{8\pi} \int \int_{-\infty}^{+\infty} \int \sum_j n_j e_j \frac{xy}{r^3} a^1_2 \frac{\partial^2}{\partial x \partial y} \Delta \xi_j(r) dV \\ &= \frac{a^1_2}{8\pi} \sum_j n_j e_j \int \int_{-\infty}^{\infty} \int \frac{x^2 y^2}{r^3} \frac{d^2 \Delta \xi_j(r)}{(r dr)^2} dV \end{aligned}$$

or in polar coordinates,

$$\begin{aligned} S^*_{yx} &= \frac{a^1_2}{8\pi} \sum_j n_j e_j \int_0^\infty \int_0^{2\pi} \int_0^\pi r^3 \sin^3 \theta \cos^2 \theta \sin^2 \varphi \frac{d^2 \Delta \xi_j(r)}{(r dr)^2} dr d\varphi d\theta \\ &= \frac{a^1_2}{30} \sum_j n_j e_j \int_0^\infty \frac{d^2 \Delta \xi_j(r)}{(r dr)^2} r^3 dr. \end{aligned}$$

Integrating twice by parts,

$$S^*_{yx} = \frac{a^1_2}{15} \sum_j n_j e_j \Delta \xi_j(0).$$

Here we substitute the values of $\Delta \xi_j(0)$ obtained in (3.5.16)

$$S^*_{yx} = -\frac{a^1_2}{15} \sum_j n_j e_j (B + \kappa)^{-2} j \sigma t_\sigma$$

whence, by comparison with (3.1.4)

$$\eta^* = -\frac{1}{15} \sum_j n_j e_j (B + \kappa)^{-2} j t_i \quad (3.6.2)$$

for the electrostatic contribution in viscosity.

In vector notation for convenient manipulation,

$$\eta^* = -\frac{1}{15} \mathbf{u} (B + \kappa)^{-2} \mathbf{t} \quad (3.6.3)$$

where \mathbf{u} is a vector with components $n_j e_j$.

3.7. Final Formula for Viscosity.

The mathematical details of the computation of the product (3.6.3) in the viscosity η^* have been relegated to Appendix I, in order that the continuity of the physical considerations should not be broken. Here we shall present and discuss only the results.

For the general case of a solution containing s species of ions, the electrostatic contribution to the viscosity is

$$\eta^* = \frac{1}{120 \kappa D k T} \left(\sum_i \frac{n_i e_i^2}{\omega_i} - 4 p \sum_{n=0}^{\infty} c_n q^{(n)} \right) \quad (3.7.1)$$

$$= 0.362 \left(\frac{\Gamma}{DT} \right)^{1/2} \left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4 \Gamma \sum_{n=0}^{\infty} c_n s^{(n)} \right) \quad (3.7.2)$$

where c_n , μ_i , τ , $\mathbf{s}^{(o)}$ and $\mathbf{s}^{(n)}$ are given by (3.8.25), (3.8.32), (3.8.42), (3.8.43), and (3.8.45), respectively. The second form is more convenient for practical calculations; $\Gamma_i = \sum_i \Gamma_i = \sum_i m_i z_i^2$ is total ionic strength (3.8.31), z_i is valence, m_i is concentration in mols per liter and Λ_i is equivalent conductance measured in ordinary units ($\text{ohm}^{-1} \text{cm}^2$ per equiv.). The second term in the brackets is a correction term involving the second power of the difference in mobilities of various ions; formulas for its exact computation are given in the appendix (3.8.27) and (3.8.44). The first term, proportional to an average fractional coefficient

$$\bar{\rho} = (\sum_i n_i e_i^2 \rho_i) / (\sum_i n_i e_i^2)$$

is dominant except when the ρ 's exhibit great (relative) differences. This observation, first made by Falkenhagen for the simple electrolyte, is hereby extended to the general case. In (3.7.2), the terms in the brackets do not contain the concentrations except as ratios; the whole effect is therefore *proportional to the square root of the concentration for a given mixture of ions*. In this regard, then, we again corroborate Falkenhagen's result for a simple electrolyte.

When $\omega_1 = \omega_2 = \dots = \omega_s = \omega$, the correction term vanishes, and we obtain

$$\eta^* = \frac{\kappa}{480\pi\omega} \quad (3.7.3)$$

which, except for a factor of 60 is the result of our preliminary calculations in §3.1. This result may be given an interesting form by substituting the Stokes formula for the coefficient of friction of a spherical particle:

$$\rho = 6\pi\eta r$$

where r is the apparent radius of the ion.

Then

$$\frac{\eta^*}{\eta} = \frac{\kappa r}{\omega} = \frac{\eta - \eta^0}{\eta}, \quad (3.7.4)$$

which shows that in the first approximation the relative change in viscosity is proportional to the ratio between the radius of an ion and that of its atmosphere.

The case of two ions having materially different mobilities has been discussed by Falkenhagen. We have calculated numerically one example of a mixture containing 3 ions, namely H^+ , K^+ and Cl^- in water at 25° ($\Lambda = 349.7, 73.5, 76.3$, respectively). Fig. 3 gives η^* as a function of μ_1 , the ratio of H^+ concentration to *total* ion concentration ($\text{H}^+ + \text{K}^+ + \text{Cl}^-$), the latter constant at 0.2 normal. For comparison, $\eta^0 = 8950 \times 10^{-6}$.

3.8. Appendix I. Discussion of Matrices.

a) Characteristic Numbers and Vectors.

We must now consider the properties of the matrices A and B and, in particular, convert the operator $(\mathbf{B} + \kappa)^{-2}$ into a convenient form for manipu-

lation. The final result for the latter step will give the viscosity as an explicit term in ionic strengths and mobilities, plus a correction term which will depend on the *square* of the *difference* in mobilities of the various ions present. In order to discuss the matrix A conveniently, we shall first transform it into a symmetrical matrix K : if we then consider the elements k_{ji} of the latter as the coefficients of a quadratic form $K(x, x)$, we may apply the well-known theory¹ of orthogonal transformations of quadratic forms.

The general element of A (3.5.1) was defined as

$$a_{ji} = \frac{4\pi}{DkT} \left(\delta_{ji} \sum_k \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \right).$$

By means of the transformation

$$\begin{aligned} K &= RAR^{-1}, \quad (A = R^{-1}KR) \\ r_{ji} &= \delta_{ji} \sqrt{n_j / \omega_j} \end{aligned} \quad (3.8.1)$$

we obtain the symmetrical matrix K with

$$k_{ji} = k_{ij} = \sqrt{a_{ji}a_{ij}} = \frac{4\pi}{DkT} \left(\delta_{ij} \sum_k \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{e_i e_j \sqrt{n_i n_j \omega_i \omega_j}}{\omega_i + \omega_j} \right) \quad (3.8.2)$$

The theory of quadratic forms assures that K may be transformed to a diagonal matrix D by means of the linear orthogonal operator² L

$$D = LKL' = LRAR^{-1}L' \quad (3.8.3)$$

where the transformation $LR = T$ exists and the result D of the operation (3.8.3) is unique. Then, since the properties of a (symmetrical) matrix are best discussed by considering the diagonal matrix obtained from it by an orthogonal transformation, we shall investigate the elements of D , i.e. the characteristic numbers $\alpha_1, \alpha_2, \dots, \alpha_n$.

We first prove that K is positive definite and hence that all the characteristic numbers $\alpha_1, \dots, \alpha_n$ are positive (whereby our previous assertion that A

¹ The first chapter of Courant & Hilbert's *Mathematische Physik* contains in compact form all the theory we shall require. Excellent, less compressed presentations are found in A. March: "Die Grundlagen der Quantenmechanik," Chapter IV (1931), and E. Wigner: "Gruppentheorie," Chapters I-III (1931).

² A diagonal matrix has all elements zero except those on the diagonal. The operator L satisfies the following conditions (cf. Courant and Hilbert):

$$\begin{aligned} L L' &= L' L = E \text{ or } L' = L^{-1} \\ \text{i.e., } l_{p\sigma} l_{q\sigma} &= \delta_{pq} \text{ and } l_{\sigma p} l_{\sigma q} = \delta_{pq}. \end{aligned} \quad (3.8.3b)$$

It converts the quadratic form $K(x, x) = k_{\sigma\tau} x_\sigma x_\tau$ into a sum of squares $K(x, x) = \alpha_\sigma y_\sigma y_\sigma$ by the linear transformation

$$x_i = l_{i\sigma} y_\sigma$$

of the variables x_i . The coefficients α_j are called the characteristic numbers of the matrix K and are the diagonal elements of $D = (\delta_{ji} \alpha_j)$. They may be found as the roots of

$$\begin{vmatrix} k_{11} - \alpha & k_{12} & \cdot & \cdot & \cdot & k_{1n} \\ k_{21} & k_{22} - \alpha & \cdot & \cdot & \cdot & k_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ k_{n1} & k_{n2} & \cdot & \cdot & \cdot & k_{nn} - \alpha \end{vmatrix} = 0$$

has real square roots, one of which (B) has only positive characteristic numbers, is justified). The quadratic form corresponding to K is

$$\frac{DkT}{4\pi} K(x, x) = \sum_{jk} \frac{n_k e_k^2 \omega_k^2}{\omega_k + \omega_j} x_j^2 + \sum_{ji} \frac{\sqrt{n_i n_j \omega_i \omega_j} e_i e_j x_i x_j}{\omega_i + \omega_j}$$

which by renaming the index k of the double summation may be written

$$\frac{DkT}{4\pi} K(x, x) = \sum_{ji} \frac{n_i e_i^2 \omega_i x_j^2 + \sqrt{n_j \omega_j} e_j \sqrt{n_i \omega_i} e_i x_j x_i}{\omega_i + \omega_j}$$

A rearrangement of terms permitted by the double summation leads to

$$\begin{aligned} \frac{DkT}{4\pi} K(x, x) &= \sum_{ij} \frac{n_j e_j^2 \omega_j x_i^2 + 2 \sqrt{n_j \omega_j} e_j \sqrt{n_i \omega_i} e_i x_j x_i + n_i e_i^2 \omega_i x_j^2}{2(\omega_i + \omega_j)} \\ &= \sum_{ij} \frac{(\sqrt{n_j \omega_j} e_j x_i + \sqrt{n_i \omega_i} e_i x_j)^2}{2(\omega_i + \omega_j)} \\ &\geq \sum_j \frac{(2 \sqrt{n_j \omega_j} e_j x_j)^2}{4\omega_j} \\ &> 0 \text{ always.} \end{aligned}$$

Thus $K(x, x)$ is positive definite and its characteristic numbers satisfy

$$\alpha_1 \geq \alpha_2 \geq \dots \geq \alpha_s > 0. \quad (3.8.4)$$

We next prove that

$$\kappa^2 = \frac{4\pi}{DkT} \sum_i n_i e_i^2 \quad (3.8.4b)$$

is a characteristic number, and, in fact, is greater than any of the others.

$$\begin{aligned} \frac{DkT}{4\pi} (K(x, x) - \kappa^2 E(x, x)) &= \sum_{jk} \frac{n_k e_k^2 \omega_k}{\omega_j + \omega_k} x_j^2 + \\ &\quad \sum_{ji} \frac{\sqrt{n_j n_i \omega_j \omega_i} e_i e_j x_j x_i}{\omega_i + \omega_j} - \sum_{ji} n_i e_i^2 x_j^2 \\ &= - \sum_{ji} \frac{(\sqrt{n_i \omega_i} e_i x_j - \sqrt{n_j \omega_j} e_j x_i)^2}{2(\omega_i + \omega_j)} \\ &\leq 0 \end{aligned}$$

is never positive and is at most zero, which can occur only when

$$\begin{aligned} \frac{x_j}{e_j \sqrt{n_j / \omega_j}} &= \frac{x_i}{e_i \sqrt{n_i / \omega_i}} \\ x_j = l_j &= \frac{e_j \sqrt{n_j \omega_j}}{(\sum_i n_i e_i^2 / \omega_i)^{1/2}} \end{aligned} \quad (3.8.5)$$

giving the normalized eigenvector¹ \mathbf{l}_1 corresponding to the characteristic value $\alpha_1 = \kappa^2$.

Thus we have shown that among the characteristic numbers

$$\alpha_1 - \kappa^2, \alpha_2 - \kappa^2, \dots, \alpha_s - \kappa^2$$

of the quadratic form

$$K(x, x) - \kappa^2 E(x, x)$$

one and only one is zero, the others negative;

$$0 = \alpha_1 - \kappa^2 > \alpha_2 - \kappa^2 \geq \dots \geq \alpha_s - \kappa^2$$

or, combining this result with (3.8.4)

$$\kappa^2 = \alpha_1 > \alpha_2 \geq \dots \geq \alpha_s > 0. \quad (3.8.6)$$

b) *Simplification of the Formula for Viscosity.*

We now turn to the practical problem of calculating the expression (3.6.3) for the viscosity:

$$\eta^* = -\frac{1}{15} \mathbf{u} (\mathbf{A}^{1/2} + \kappa)^{-2} \mathbf{t}. \quad (3.8.7)$$

Since matrix relations like $A + B = C$ and $AB = F$ are invariant against transformations of the type

$$A \rightarrow T A T^{-1}, \text{ e.g.}$$

$$T A T^{-1} T B T^{-1} = T(AB)T^{-1},$$

we may express our formula (3.8.7) for viscosity as follows:

$$-15\eta^* = \mathbf{u} \mathbf{R}^{-1} (\mathbf{K}^{1/2} + \kappa)^{-2} \mathbf{R} \mathbf{t} \quad (3.8.8)$$

$$= \mathbf{u} \mathbf{R}^{-1} \mathbf{L}' (\mathbf{D}^{1/2} + \kappa)^{-2} \mathbf{L} \mathbf{R} \mathbf{t}. \quad (3.8.9)$$

It is impossible in general to obtain an explicit expression for the transformation L and for the characteristic values $\alpha_1, \dots, \alpha_s$. However, the knowledge of α_1 and the corresponding eigenvector (3.8.5) will enable us to isolate a term that yields the major contribution to the final result, and to simplify the calculation of the remainder.

This simplification depends on a relation between the rather complicated vector \mathbf{Rt} and a vector \mathbf{m}

$$m_j = \frac{e_j}{\omega_j} \sqrt{\frac{n_j}{\omega_j}} \quad (3.8.10)$$

which appeared during a systematic study of the product in (3.8.7). The components of \mathbf{Rt} are, by (3.8.1) and (3.5.2)

$$R_{jj}t_j = -\frac{4\pi}{\kappa(DkT)^2} e_j \sqrt{\frac{n_j}{\omega_j}} \sum_i \frac{n_i e_i^2}{\omega_i + \omega_j}. \quad (3.8.11)$$

¹ That is, the vector such that $\mathbf{Kx} = \alpha_1 \mathbf{x}$, i.e. operation on \mathbf{x} with \mathbf{K} is equivalent to multiplying \mathbf{x} with the (scalar) characteristic number $\alpha_1 = \kappa^2$. The components l_{1j} of \mathbf{l}_1 are the elements of the first row of L .

The scalar product¹ of \mathbf{Rt} and the eigenvector \mathbf{l}_1 is

$$\begin{aligned} (\mathbf{l}_1 \mathbf{Rt}) &= -\frac{4\pi}{\kappa(DkT)^2} \sum_j e_j \sqrt{\frac{n_j}{\omega_j}} e_j \sqrt{\frac{n_j}{\omega_j}} \frac{n_i e_i^2}{\omega_i + \omega_j} / \left(\sum_k \frac{n_k e_k^2}{\omega_k} \right)^{1/2} \\ &= -\frac{4\pi}{\kappa(DkT)^2} \sum_j \frac{n_j e_j^2 n_i e_i^2}{\omega_j (\omega_i + \omega_j)} / \left(\sum_k \frac{n_k e_k^2}{\omega_k} \right)^{1/2} \\ &= -\frac{2\pi}{\kappa(DkT)^2} \left(\sum_i \frac{n_i e_i^2}{\omega_i} \right)^{3/2} \end{aligned} \quad (3.8.12)$$

and then the part of \mathbf{Rt} that is "parallel" \mathbf{l}_1 is given by

$$(\mathbf{l}_1 \mathbf{Rt}) \mathbf{l}_1 = -\frac{2\pi}{\kappa(DkT)^2} e_j \sqrt{\frac{n_j}{\omega_j}} \sum_i \frac{n_i e_i^2}{\omega_i}. \quad (3.8.13)$$

The remainder of \mathbf{Rt} with the components

$$\begin{aligned} R_{jj} t_j - (\mathbf{l}_1 \mathbf{Rt}) l_{1j} &= -\frac{4\pi}{\kappa(DkT)^2} e_j \sqrt{\frac{n_j}{\omega_j}} \sum_i n_i e_i^2 \left(\frac{1}{\omega_i + \omega_j} - \frac{1}{2\omega_i} \right) \\ &= \frac{2\pi}{\kappa(DkT)^2} e_j \sqrt{\frac{n_j}{\omega_j}} \sum_i \frac{n_i e_i^2}{\omega_i} \frac{\omega_j - \omega_i}{\omega_j + \omega_i} \end{aligned} \quad (3.8.14)$$

is "perpendicular" to \mathbf{l}_1 , i.e.

$$(\mathbf{l}_1 \{ \mathbf{Rt} - (\mathbf{l}_1 \mathbf{Rt}) \mathbf{l}_1 \}) = 0.$$

Let us now evaluate $(\mathbf{K} - \kappa^2) \mathbf{m}$:

$$\begin{aligned} \frac{DkT}{4\pi} (\mathbf{K} - \kappa^2)_{j\sigma} m_\sigma &= \sqrt{\frac{n_j}{\omega_j}} \frac{e_j}{\omega_j} \sum_i \frac{n_i e_i^2}{\omega_i + \omega_j} + \sum_i \sqrt{\frac{n_i}{\omega_i}} \frac{e_i}{\omega_i} \frac{e_j e_i}{\omega_i + \omega_j} \sqrt{\frac{n_j n_i \omega_j \omega_i}{\omega_i + \omega_j}} \\ &\quad - \sqrt{\frac{n_j}{\omega_j}} \frac{e_j}{\omega_j} \sum_i n_i e_i^2 \\ &= e_j \sqrt{\frac{n_j}{\omega_j}} \sum_i \frac{n_i e_i^2}{\omega_i} \frac{\omega_j - \omega_i}{\omega_j + \omega_i} \end{aligned} \quad (3.8.15)$$

By comparing (3.8.14) and (3.8.15), it is immediately apparent that

$$\begin{aligned} \mathbf{Rt} - (\mathbf{l}_1 \mathbf{Rt}) \mathbf{l}_1 &= \frac{1}{2\kappa DkT} (\mathbf{K} - \kappa^2) \mathbf{m}, \text{ or} \\ \mathbf{Rt} &= \frac{1}{2\kappa DkT} (\mathbf{K} - \kappa^2) \mathbf{m} + (\mathbf{l}_1 \mathbf{Rt}) \mathbf{l}_1. \end{aligned} \quad (3.8.16)$$

The vector \mathbf{Rt} is thus expressed in terms of the vector \mathbf{m} and the eigenvector \mathbf{l}_1 . This result substituted in (3.8.8) gives

¹ We use the conventional notation (\mathbf{a}, \mathbf{b}) to denote the scalar product $a_\sigma b_\sigma$ of two vectors.

$$\begin{aligned}
 -15\eta^* &= \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-2} \left(\frac{(\mathbf{K} - \kappa^2) \mathbf{m}}{2\kappa DkT} + (1_1 \mathbf{Rt}) 1_1 \right) \\
 &= \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-2} (1_1 \mathbf{Rt}) 1_1 + \frac{1}{2\kappa DkT} \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-1} (\mathbf{K}^{1/2} - \kappa) \mathbf{m}.
 \end{aligned} \tag{3.8.17}$$

Since 1_1 is the eigenvector corresponding to the characteristic number $\alpha_1 = \kappa^2$, the first term of (3.8.17),

$$(1_1 \mathbf{Rt}) \mathbf{uR}^{-1} \mathbf{L}' (\mathbf{D}^{1/2} + \kappa)^{-2} \mathbf{L} 1_1$$

reduces to $(1_1 \mathbf{Rt}) \mathbf{uR}^{-1} \mathbf{L}' (\alpha_1^{1/2} + \kappa)^{-2} \mathbf{L} 1_1 = \frac{(1_1 \mathbf{Rt})}{4\kappa^2} \mathbf{uR}^{-1} 1_1$ due to the orthogonality of the transformation L :

$$Ll_1 = l_{j\sigma} l_{1\sigma} = \delta_{j1}.$$

This term may now be readily evaluated by (3.8.12), (3.8.1), (3.8.5) and (3.8.4b).

$$\frac{(1_1 \mathbf{Rt})}{4\kappa^2} \mathbf{uR}^{-1} 1_1 = \frac{-1}{8\kappa DkT} \sum_i \frac{n_i e_i^2}{\omega_i}. \tag{3.8.18}$$

We shall show in the next paragraphs that the second term in (3.8.17) is the previously mentioned correction term. That is, the term just evaluated is the main contribution to η^* , and in fact, for the simple case where

$$\omega_1 = \omega_2 = \omega_3 \dots = \omega$$

the correction term vanishes, and

$$\eta^* = \frac{1}{120\kappa DkT} \sum_i \frac{n_i e_i^2}{\omega_i} = \frac{\kappa}{480 \pi \omega} \tag{3.8.19}$$

which is the result announced in the introduction (3.1.3).

c. *Calculation of Correction Term in (3.8.17).*

First of all, we note that the correction term

$$\begin{aligned}
 \delta\eta^* &= \frac{-1}{30\kappa DkT} \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-1} (\mathbf{K}^{1/2} - \kappa) \mathbf{m} \\
 &= \frac{-1}{30\kappa DkT} \mathbf{uR}^{-1} \mathbf{L}' (\mathbf{D}^{1/2} + \kappa)^{-1} (\mathbf{D}^{1/2} - \kappa) \mathbf{L} \mathbf{m}
 \end{aligned} \tag{3.8.20}$$

vanishes when the largest characteristic number $\alpha_1 = d_{11} = \kappa^2$ is substituted in place of \mathbf{K} . Therefore, we may add to \mathbf{m} or \mathbf{uR}^{-1} any multiple of 1_1 (since $(\mathbf{D}^{1/2} - \kappa) \mathbf{L} 1_1 = 0$ always), which will permit us to express (3.8.20) in a more convenient form for numerical computation. Thus if we define two vectors \mathbf{p} and \mathbf{q} by

$$\begin{aligned}
 q_j &= m_j - (\mathbf{m}, 1_1) l_{1j} = e_j \sqrt{\frac{n_j}{\omega_j}} \left(\frac{1}{\omega_j} - \frac{\sum_i n_i e_i^2}{\sum_i n_i e_i^2 \omega_i} \right) \\
 &= e_j \sqrt{n_j/\omega_j} (\rho_j - \bar{\rho}^2/\bar{\rho})
 \end{aligned} \tag{3.8.21}$$

and

$$\begin{aligned}
 p_j &= u_j R^{-1}_{jj} - (\mathbf{uR}^{-1} 1_1) l_{1j} = e_j \sqrt{n_j \omega_j} - e_j \sqrt{n_j/\omega_j} \sum_i n_i e_i^2 / \sum_i n_i e_i^2 / \omega_i \\
 &= e_j \sqrt{n_j/\omega_j} (1/\rho_j - 1/\bar{\rho}),
 \end{aligned} \tag{3.8.22}$$

\mathbf{p} and \mathbf{q} may replace \mathbf{m} and \mathbf{uR}^{-1} in (3.8.20) without changing the latter. The symbols $\bar{\rho}$ and $\bar{\rho}^2$ are obvious abbreviations for the averages of $\rho_j = 1/\omega_j$ and ρ_j^2 , averaged with respect to the ionic strength. For the case when all the mobilities are equal, (3.8.21) and (3.8.22) vanish and the correction term becomes zero; this fact is also clear from (3.8.5) and (3.9.10), which show that for this case, \mathbf{m} becomes proportional to the eigenvector $\mathbf{1}_1$, and then $(\mathbf{D}^{1/2} - \kappa)\mathbf{Lm}$ vanishes. Introducing the results of the above steps

$$\begin{aligned}\delta\eta^* &= \frac{-1}{30 \kappa D k T} \mathbf{p}(\mathbf{K}^{1/2} + \kappa)^{-1} (\mathbf{K}^{1/2} - \kappa) \mathbf{q} \\ &= \frac{-1}{30 \kappa D k T} \mathbf{p} (1 - 2 \{1 + \kappa^{-1} \mathbf{K}^{1/2}\}^{-1}) \mathbf{q}.\end{aligned}\quad (3.8.23)$$

d) *Power Series Expansion.*

As a starting-point for expanding the matrix \mathbf{K} in a power series, we note that a function

$$f(D) \equiv \begin{pmatrix} f(\alpha_1) & 0 & . & . & . & 0 \\ 0 & f(\alpha_2) & . & . & . & 0 \\ . & . & . & . & . & . \\ 0 & . & 0 & . & f(\alpha_s) & . \end{pmatrix}$$

of the diagonal matrix

$$D = \begin{pmatrix} \alpha_1 & . & . & . & . & 0 \\ 0 & \alpha_2 & . & . & . & 0 \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & \alpha_s \end{pmatrix} = (\alpha_j \delta_{jl})$$

may be expanded in a Taylor series by expanding the elements

$$f(\alpha_j) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (\alpha_j - a)^n = \sum_{n=0}^{\infty} c_n (\alpha_j - a)^n$$

provided that this series converges for $\alpha_j = \alpha_1, \dots, \alpha_s$. The series may be written in matrix form

$$f(\mathbf{D}) = \sum_{n=0}^{\infty} c_n (\mathbf{D} - a \mathbf{1})^n.$$

Now if

$$\mathbf{K} = \mathbf{L}^{-1} \mathbf{D} \mathbf{L},$$

(where, if \mathbf{L} be orthogonal, $\mathbf{L}^{-1} = \mathbf{L}'$), and if we adopt the evidently self-consistent definition of a matrix function

$$f(\mathbf{K}) = \mathbf{L}^{-1} f(\mathbf{D}) \mathbf{L},$$

whereby e.g.

$$\mathbf{K}^n = \mathbf{L}^{-1} \mathbf{D}^n \mathbf{L}$$

we shall have

$$f(\mathbf{K}) = \mathbf{L}^{-1} f(\mathbf{D}) \mathbf{L} = \sum_{n=0}^{\infty} c_n (\mathbf{K} - a \mathbf{1})^n,$$

provided that this series converges for every characteristic number of \mathbf{K} , substituted in the place of \mathbf{K} . We are particularly interested in the function

$$f(\kappa^{-2} \mathbf{K}) = 1 - 2(1 + \kappa^{-1} \mathbf{K}^{1/2})^{-1}. \quad (3.8.24)$$

The Taylor expansion of $f(z)$ around $a = 1/2$ is, with

$$z = \frac{1}{2} + t; t = 2z - 1$$

$$\begin{aligned} (1 + \sqrt{z})^{-1} &= (1 - z)^{-1} - \sqrt{z} (1 - z)^{-1} \\ &= 2(1 - 2t)^{-1} - \sqrt{2} (1 + 2t)^{1/2} (1 - 2t)^{-1} \\ &= \sqrt{2} \left\{ \sqrt{2} \sum_{n=0}^{\infty} (2t)^n - \sum_{p=0}^{\infty} \binom{1/2}{p} (2t)^p \sum_{q=0}^{\infty} (2t)^q \right\} \\ &= \sqrt{2} \left\{ \sqrt{2} \sum_{n=0}^{\infty} (2t)^n - \sum_{n=0}^{\infty} (2t)^n \sum_{p=0}^n \binom{1/2}{p} \right\} \\ &= \sum_{n=0}^{\infty} \sqrt{2} \left\{ \sqrt{2} - \sum_{p=0}^n \binom{1/2}{p} \right\} (2z - 1)^n \end{aligned}$$

or with

$$\begin{aligned} c_0 &= 1 - 2\sqrt{2}(\sqrt{2} - 1) = -3 + 2\sqrt{2} \\ c_n &= -2\sqrt{2} \left\{ \sqrt{2} - \sum_{p=0}^n \binom{1/2}{p} \right\}, n \geq 1 \\ 1 - 2(1 + \sqrt{z})^{-1} &= \sum_{n=0}^{\infty} c_n (2z - 1)^n \end{aligned} \quad (3.8.25)$$

$$c_0 = -0.1716 \quad c_3 = 0.0659$$

$$c_1 = 0.2427 \quad c_4 = -0.0447$$

$$c_2 = -0.1109 \quad c_5 = 0.0325$$

convergent in the interval $0 \leq z \leq 1$.

According to (3.8.6), the characteristic numbers $\alpha_1/\kappa^2, \dots, \alpha_s/\kappa^2$ of our matrix $\kappa^{-1}\mathbf{K}$ are all in this range. Of course, for the largest, $\alpha_1 = \kappa^2$, the convergence will be slow; however, the vector $\mathbf{q} = \mathbf{m} - l_1(l_1\mathbf{m})$, to which the operator series will be applied, is orthogonal to l_1 , so that the misbehavior of α_1 in the expansion

$$\sum_{n=0}^{\infty} c_n (2\kappa^{-2}\mathbf{K} - 1)^n \mathbf{q} = \sum_{n=0}^{\infty} c_n \sum_{p=1}^s l_p (2\kappa^{-2}\alpha_p - 1)^n (l_p, \mathbf{q}) \quad (3.8.26)$$

is harmless, because the corresponding terms never enter. The remaining characteristic numbers $\alpha_2, \dots, \alpha_s$ are ordinarily close enough to $\kappa^2/2$ for the series to converge rapidly.

If we introduce the series expansion (3.8.26) into the correction term (3.8.23), we obtain

$$\begin{aligned} \delta\eta^* &= \frac{-1}{30\kappa DkT} p \sum_{n=0}^{\infty} c_n (2\kappa^{-2}\mathbf{K} - 1)^n \mathbf{q} \\ &= \frac{-1}{30\kappa DkT} p \sum_{n=0}^{\infty} c_n \mathbf{q}^{(n)} \end{aligned} \quad (3.8.27)$$

where $\mathbf{q}^{(n)}$ is given by the recursion formula

$$\mathbf{q}^{(0)} = \mathbf{q}$$

$$\mathbf{q}^{(n)} = (2\kappa^{-2}\mathbf{K} - 1)\mathbf{q}^{(n-1)}$$

and

$$p_i = e_i \sqrt{n_i/\omega_i} (1/\rho_i - 1/\bar{\rho})$$

$$q_i = e_i \sqrt{n_i/\omega_i} (\rho_i - \bar{\rho}^2/\bar{\rho}).$$

The total electrostatic contribution to viscosity is then

$$\eta^* = \frac{1}{120\kappa DkT} \left(\sum_i \frac{n_i e_i^2}{\omega_i} - 4(\mathbf{p}, \left\{ \sum_{n=0}^{\infty} c_n \mathbf{q}^{(n)} \right\}) \right). \quad (3.8.28)$$

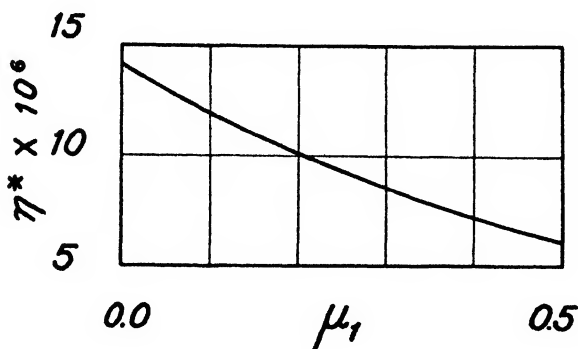


FIG. 3

Electrostatic Contribution to Viscosity of HCl-KCl Mixtures

e) *Calculation for a Simple Electrolyte.*

For $s = 2$, our formula (3.8.17) gives the result obtained by Falkenhagen. The characteristic values of \mathbf{K} , obtained by solving the secular equation, are

$$\alpha_1 = \kappa^2, \alpha_2 = q\kappa^2,$$

where

$$q = \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{(n_1 e_1^2 + n_2 e_2^2)(\omega_1 + \omega_2)}. \quad (3.8.29)$$

Now in evaluating our viscosity formula

$$\eta^* = \frac{1}{120\kappa DkT} \left(\frac{n_1 e_1^2}{\omega_1} + \frac{n_2 e_2^2}{\omega_2} - 4\mathbf{p} \left(1 - \{2\kappa^{-1}\mathbf{K} + 1\}^{-1} \right) \mathbf{q} \right),$$

we remember that \mathbf{q} is orthogonal to \mathbf{l}_1 , which means parallel to \mathbf{l}_2 . Consequently,

$$f(\mathbf{K})\mathbf{q} = f(\alpha_2)\mathbf{q}$$

and the correction term becomes

$$-4\mathbf{p}f(\alpha_2)\mathbf{q} = -4f(\alpha_2)(\mathbf{p}, \mathbf{q})$$

Substituting our values

$$f(\alpha_2) = \frac{q - 1}{(\sqrt{q} + 1)^2}$$

$$(\mathbf{p}, \mathbf{q}) = \frac{-n_1 e_1^2 n_2 e_2^2 (\omega_1 - \omega_2)^2}{(n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1) \omega_1 \omega_2}$$

whence

$$-4 f(\alpha_2) (\mathbf{p}, \mathbf{q}) = \frac{-4 n_1 e_1^2 n_2 e_2^2 (\omega_1 - \omega_2)^2}{(n_1 e_1^2 + n_2 e_2^2) (\omega_1 + \omega_2) (\omega_1 \omega_2) (\sqrt{q} + 1)^2}$$

$$= \frac{-4 z_1 z_2 (\rho_2 - \rho_1)^2}{(\sqrt{q} + 1)^2 (z_1 + z_2)^2 (\rho_1 + \rho_2)}$$

where z_1 and z_2 are the valences of the ions.

Then

$$\eta^* = \frac{\kappa}{480\pi} \left((1 - q) (\rho_1 + \rho_2) - \frac{4}{(\sqrt{q} + 1)^2} \frac{z_1 z_2}{(z_1 + z_2)^2} \frac{(\rho_2 - \rho_1)^2}{(\rho_1 + \rho_2)} \right) \quad (3.8.30)$$

f) *Conversion to Practical Units.*

Numerical computation of η^* by the formula (3.8.17) is simplified by introducing the ionic strength

$$\Gamma_i = m_i z_i^2 = \frac{1000}{N\epsilon^2} n_i e_i^2, \quad (3.8.31)$$

where m_i is concentration in mols per liter and z_i is the valence. (N = Avogadro's number, ϵ = electronic charge). We define the relative ionic strength μ_i by

$$\mu_i = \frac{\Gamma_i}{\Gamma} = \frac{n_i e_i^2}{\sum_i n_i e_i^2} \quad (3.8.32)$$

so that

$$\kappa^2 = \frac{N^2 \epsilon^2}{1000} \frac{4\pi}{DRT} \Gamma. \quad (3.8.33)$$

Then by the transformation

$$\mathbf{M} \mathbf{K} \mathbf{M}^{-1} = \mathbf{G}'$$

$$m_{ji} = \delta_{ji} e_j \sqrt{n_j \omega_j} \quad (3.8.34)$$

we obtain a new matrix¹ \mathbf{G}' with elements

$$g'_{ji} = \frac{4\pi}{DkT} \left(\delta_{ji} \sum_i n_i e_i^2 \frac{\omega_i}{\omega_i + \omega_j} + n_j e_j^2 \frac{\omega_j}{\omega_i + \omega_j} \right).$$

Then since $\kappa^{-2} \mathbf{K}$ appears in (3.8.26), we introduce a new matrix \mathbf{H}' whose elements are pure numbers

¹ We write $\mathbf{G}' = (g'_{ji}) = (g_{ij})$ for this matrix, because the transposed matrix $\mathbf{G} = (g_{ji})$ appears in the conductance problem, and will be used more frequently.

$$h'_{ji} = \frac{g'_{ji}}{\kappa^2} = \left(\delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_j \frac{\omega_j}{\omega_i + \omega_j} \right). \quad (3.8.35)$$

Now ρ_j was defined as the friction coefficient for an ion of the j -th species, so that

$$\frac{1}{\rho_j} = \omega_j = \frac{u_j}{|e_j|}. \quad (3.8.36)$$

where u_j is the mobility per unit field in electrostatic units. The mobility \bar{u}_j for a field of one volt per centimeter is accordingly $u_j/300$ and

$$\omega_j = \frac{300 \bar{u}_j}{\epsilon z_j} \quad (3.8.37)$$

If Λ_j is the equivalent conductance,

$$\Lambda_j = 96\,500 \bar{u}_j \quad (3.8.39)$$

and

$$\omega_j = \frac{300}{96\,500} \frac{\Lambda_j}{z_j}; \quad (3.8.40)$$

also

$$\frac{\omega_i}{\omega_i + \omega_j} = \frac{\Lambda_i/z_i}{\Lambda_i/z_i + \Lambda_j/z_j}, \text{ a pure number.} \quad (3.8.41)$$

Then

$$h'_{ji} = \delta_{ji} \sum_i \mu_i \frac{\Lambda_i/z_i}{\Lambda_i/z_i + \Lambda_j/z_j} + \mu_j \frac{\Lambda_j/z_j}{\Lambda_i/z_i + \Lambda_j/z_j}.$$

If we now apply the transformation (3.8.34) to (3.8.27), and substitute (3.8.35), we obtain

$$\mathbf{p} \sum_{n=0}^{\infty} c_n (2\kappa^{-2} \mathbf{K} - 1)^n \mathbf{q} = \mathbf{p} \mathbf{M}^{-1} \sum_{n=0}^{\infty} c_n (2\mathbf{H}' - 1) \mathbf{M} \mathbf{q},$$

where

$$(\mathbf{pM}^{-1})_j = \frac{\bar{\rho} - \rho_j}{\rho}$$

and

$$(\mathbf{Mq})_j = n_j e_j^2 (\rho_j - \bar{\rho}^2/\rho) = \frac{DkT\kappa^2}{4\pi} \mu_j (\rho_j - \bar{\rho}^2/\rho).$$

This may be simplified by defining two new vectors

$$r_j = 1 - \rho_j/\bar{\rho} = 1 - \frac{z_j/\Lambda_j}{z/\Lambda} \quad (3.8.42)$$

$$s_j = \mu_j \left(z_j/\Lambda_j - \overline{(z/\Lambda)^2} / (z/\Lambda) \right), \quad (3.8.43)$$

for then

$$\delta\eta' = \frac{-\kappa}{120\pi} \frac{96\,500}{300} \epsilon \Gamma \sum_{n=0}^{\infty} c_n \mathbf{s}^{(n)} \quad (3.8.44)$$

where $\mathbf{s}^{(n)}$ is defined by the recursion formula

$$\mathbf{s}^{(0)} = \mathbf{s}; \mathbf{s}^{(n)} = (2\mathbf{H}' - 1) \mathbf{s}^{(n-1)}. \quad (3.8.45)$$

Combining the values for the two terms of η^* ,

$$\eta^* = \frac{\kappa}{480\pi} \frac{96500 \epsilon}{300} \left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4r \sum_{n=0}^{\infty} c_n \mathbf{s}^{(n)} \right), \quad (3.8.46)$$

which on substituting (3.8.33) for κ becomes

$$\begin{aligned} \eta^* &= \frac{965 \text{ N}\epsilon^2}{144 \sqrt{250\pi}} \sqrt{\frac{\Gamma}{DRT}} \left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4r \sum_{n=0}^{\infty} c_n \mathbf{s}^{(n)} \right) \\ &= 0.362 \left(\frac{\Gamma}{DT} \right)^{1/2} \left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4r \sum_{n=0}^{\infty} c_n \mathbf{s}^{(n)} \right). \end{aligned} \quad (3.8.47)$$

3.9. Appendix II. Mechanism of Force Transfer.

a) Statement of Problem.

In our preliminary discussion (§3.1), we showed that a velocity gradient in a flowing electrolyte produced a stationary deformation of the ionic atmospheres on account of the finite time of relaxation of the latter, and that an additional force transfer between volume elements appeared, due to the resulting asymmetry of the potentials of the ionic atmospheres. We then demonstrated that this additional force corresponds to an increase in the force per unit volume:

$$\mathbf{F}^* = \eta^* \Delta \mathbf{v}. \quad (3.9.1)$$

Now if our assumptions have been consistent, this force should be derivable from the potentials ψ_j ; the x component of the force acting on a j -ion due to the asymmetry of its atmosphere is

$$-e_j \left(\frac{\partial \psi'_j}{\partial x} \right)_{r=0}$$

and therefore the net force per unit volume containing n_j ions of species 1, . . . , s is

$$\mathbf{F}^*_x = - \sum_j n_j e_j \left(\frac{\partial \psi'_j}{\partial x} \right)_{r=0}. \quad (3.9.2)$$

We shall calculate the potentials ψ'_j for the simple case where

$$s = 2; n_1 = n_2 = n; e_1 = -e_2 = e; \omega_1 = \omega_2 = \omega \quad (3.9.3)$$

and carry out the operations indicated in (3.9.2). The result will be identical with that obtained from (3.9.1) by substituting (3.2.2) for the velocity:

$$\mathbf{F}^*_x = b^1_{\mu\mu} \eta^* \quad (3.9.4)$$

and we shall have gained exact information concerning the transfer of stress by the interionic forces.

We recall that the potential ψ'_j was given by

$$\psi'_j(r_1, r_{12}) = b_{\mu\mu}^\lambda D_\lambda v_j(r) + c_{\nu\nu}^\mu D_{\mu\nu}^2 \xi_j(r) + \frac{1}{2} b_{\mu\nu}^\lambda D_{\lambda\mu\nu}^3 v_j(r). \quad (3.9.5)$$

The even part of the potential $\xi_j(r)$ has already been determined for the general case (3.5.13); we shall first compute its value for our special case (3.9.3), and then the functions $u_j(r)$ and $v_j(r)$ must be obtained by solving (3.4.4) and (3.4.6).

b) *Distribution Functions and Potentials.*

According to (3.5.13) and (3.8.3)

$$\xi_j(r) = \{\chi(r, B)\}_{j\sigma} t_\sigma = T^{-1}_{j\mu} \{\chi(r, D)\}_\mu T_{\mu\sigma} t_\sigma \quad (3.9.6)$$

where the matrix D (cf. 3.8.29) is

$$D = \begin{pmatrix} \kappa^2 & 0 \\ 0 & \kappa^2/2 \end{pmatrix}.$$

In order to obtain $T = LR$, we take from (3.8.5) the components of the eigenvector 1_1

$$l_{1j} = e_j/\sqrt{2e^2}; \quad l_{11} = 1/\sqrt{2}, \quad l_{12} = -1/\sqrt{2}$$

and from the symmetry and orthogonality conditions (3.8.3b),

$$l_{22} = -l_{11} = -1/\sqrt{2} \quad \text{and} \quad l_{21} = l_{12} = -1/\sqrt{2}$$

so that

$$L = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ -1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}.$$

Then since $T = LR$, i.e. $t_{ij} = l_{i\sigma} r_{\sigma j} = \sqrt{n/\omega} l_{ij}$ and $TT^{-1} = 1$,

$$T = \begin{pmatrix} \sqrt{\frac{n}{2\omega}} & -\sqrt{\frac{n}{2\omega}} \\ -\sqrt{\frac{n}{2\omega}} & -\sqrt{\frac{n}{2\omega}} \end{pmatrix}, \quad T^{-1} = \begin{pmatrix} \sqrt{\frac{\omega}{2n}} & -\sqrt{\frac{\omega}{2n}} \\ -\sqrt{\frac{\omega}{2n}} & -\sqrt{\frac{\omega}{2n}} \end{pmatrix}.$$

The components of t are

$$t_1 = \frac{-\kappa e}{2\omega DkT} = -t_2.$$

On substituting these values in (3.9.6), we obtain

$$\xi_j(r) = \frac{-\kappa e_j}{2\omega DkT} \chi(r, \kappa^2).$$

The expression $\chi(r, \beta^2)$ given in (3.5.10) becomes indeterminate for $\beta^2 = \kappa^2$, but may be immediately evaluated by noting that

$$\lim_{\beta \rightarrow \kappa} \frac{\partial}{\partial \kappa} \left(\frac{f(\beta) - f(\kappa)}{\beta - \kappa} \right) = \frac{1}{2} \frac{\partial^2 f(\kappa)}{\partial \kappa^2}$$

whence

$$\xi_j(r) = \frac{-e_j \kappa}{4\omega DkT} \frac{\partial}{\partial \kappa} \left(\frac{e^{-\kappa r} - 1}{\kappa^4 r} + \frac{e^{-\kappa r}}{2 \kappa^3} \right) = \frac{-e_j \kappa}{2 \omega DkT} X(r). \quad (3.9.7)$$

The term in $\left(\frac{\partial \psi'_j}{\partial q^m}\right)$ corresponding to $\xi_j(r)$ is found to be

$$(c^\mu_m q^\mu + c^m_\nu q^\nu) \frac{d^2 \xi_j}{(r dr)^2} + c^\mu_\nu q^\mu q^\nu \frac{d^3 \xi_j(r)}{(r dr)^3} \quad (3.9.8)$$

by carrying out the differentiation indicated by $D^3_{\mu\nu m}$ and noting the relations (3.2.4). This contribution to the directed force should vanish because it is due to the part of the potential that is even in the coordinates, and indeed, since

$$\frac{d^2 X(r)}{(r dr)^2} = \frac{1}{4} \sum_{n=0}^{\infty} \frac{(-\kappa)^n r^n}{n! (n+5)}$$

and

$$\frac{d^3 X(r)}{(r dr)^3} = \frac{1}{4} \sum_{n=0}^{\infty} \frac{(-\kappa)^{n+1} r^{n+1}}{n! (n+6)}$$

we see that this is actually the case in the limit $r = 0$ (and of course $q = 0$) in (3.9.8): the first term is of the order $q \sim r$ and the second of the order r^2 .

By means of the corresponding term in the Poisson equation, F_{ji} is eliminated from (3.4.6), giving

$$\begin{aligned} b^\lambda_{\mu\nu} D^3_{\lambda\mu\nu} \left(\Delta \Delta u_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta u_i + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta u_i \right. \\ \left. - \frac{8\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \frac{d(r \xi_i(r))}{dr} + \frac{16\pi}{D} \sum_i \frac{e_i \omega_j}{n_j (\omega_i + \omega_j)} \varphi_{ji} \right. \\ \left. + \frac{4\pi}{DkT} \sum_i \frac{e_i \theta(r)}{n_j (\omega_i + \omega_j)} \right) = 0. \end{aligned}$$

The condition $\omega_1 = \dots = \omega_s = \omega$ permits φ_{ji} to be eliminated by means of the even term in the Poisson equation, so that

$$\begin{aligned} b^\lambda_{\mu\nu} D^3_{\lambda\mu\nu} \left(\Delta \Delta u_j - \frac{2\pi}{DkT} \sum_i n_i e_i^2 \Delta u_i + \frac{2\pi}{DkT} \sum_i n_i e_i e_j \Delta u_i \right. \\ \left. - \frac{4\pi}{DkT} \sum_i n_i e_i e_j \frac{d(r \xi_i(r))}{dr} - 2\Delta \xi_j + \frac{2\pi}{\omega DkT} \sum_i \frac{e_i \theta(r)}{n_j} \right) = 0. \quad (3.9.9) \end{aligned}$$

By differentiating (3.9.7)

$$\Delta \xi_j = \frac{-\kappa e_i}{4\omega DkT} \frac{\partial}{\partial \kappa} \left(\frac{e^{-\kappa r}}{2\kappa} \right). \quad (3.9.10)$$

Also

$$\frac{d}{dr} r \xi_i(r) = \frac{\kappa e_i}{4\omega DkT} \frac{\partial}{\partial \kappa} \left((1 + \kappa r) \frac{e^{-\kappa r}}{2\kappa^3} \right) \quad (3.9.11)$$

and by the definition in (3.2.6)

$$\theta(r) = -\frac{n_i n_j e_i e_j}{\kappa^2 DkT} \left(r e^{-\kappa r} + \frac{e^{-\kappa r}}{\kappa} \right) \quad (3.9.12)$$

(where in view of the boundary conditions discussed in §3.5, several terms have been dropped: compare with (3.4.7) and (3.4.11)). We substitute the "known" functions of r just obtained in (3.9.9), integrate, and perform the summations:

$$\begin{aligned}\Delta\Delta u_j - \frac{4\pi}{DkT} n e^2 \Delta u_j + \frac{2\pi}{DkT} n e e_j (\Delta u_1 - \Delta u_2) = \\ = \frac{3e_j}{8\omega DkT\kappa} \left(1 + r\kappa - \frac{r^2\kappa^2}{3} \right) e^{-\kappa r}.\end{aligned}$$

By giving j the values 1 and 2 and adding the resulting equations, we obtain

$$\Delta(\Delta - \kappa^2/2)(u_1 + u_2) = 0$$

whence, by integration and consideration of boundary conditions, $\Delta u_1 = -\Delta u_2$. We thus obtain as the equation determining $u_j(r)$

$$\Delta\Delta u_j = \frac{3e_j}{8\omega DkT\kappa} \left(1 + r\kappa - \frac{r^2\kappa^2}{3} \right) e^{-\kappa r}$$

which has the solution

$$\begin{aligned}u_j(r) &= \frac{3e_j}{8\omega DkT\kappa} \left[\frac{1}{\kappa^5 r} \left\{ 16 - e^{-\kappa r} \left(16 + 11\kappa r + 3\kappa^2 r^2 + \frac{\kappa^3 r^3}{3} \right) \right\} \right] \\ &= \frac{3e_j}{8\omega DkT\kappa} Y(r)\end{aligned}$$

satisfying the restrictions imposed on the potential for $r = \infty$ and $r = 0$.

The term containing $u_j(r)$ in the formula (3.9.2) for the force equals

$$\begin{aligned}\frac{1}{2} b_{\mu\nu}^{\lambda} D_{\lambda\mu\nu}^4 u_j(r) &= \frac{1}{2} b_{\mu\mu}^m \frac{d^2 u_j(r)}{(r dr)^2} + O(r^2) \frac{d^3 u_j(r)}{(r dr)^3} \\ &\quad + O(r^4) \frac{d^4 u_j(r)}{(r dr)^4}\end{aligned}$$

where the notation $O(r^2)$ means a coefficient of the order of r^2 . If, as before, we write $Y(r)$ as a series and differentiate, we find

$$\begin{aligned}\frac{d^2 Y(r)}{(r dr)^2} &= - \sum_{n=0}^{\infty} \frac{(-\kappa)^n r^n (n-1)}{n! 3(n+5)} \\ \frac{d^3 Y(r)}{(r dr)^3} &= - \sum_{n=0}^{\infty} \frac{(-\kappa)^{n+2} r^n}{n! 3(n+7)} = O(1)_{r=0}\end{aligned}$$

and

$$\frac{d^4 Y(r)}{(r dr)^4} = \sum_{n=0}^{\infty} \frac{(-\kappa)^{n+3} r^{n-1}}{n! 3(n+8)} = O(r^{-1})_{r=0}$$

so that in the limit $r = 0$, we have

$$\left(\frac{1}{2} b_{\mu\mu}^{\lambda} D_{\lambda\mu\nu}^4 u_j(r) \right)_{r=0} = b_{\mu\mu}^m \frac{e_j}{80\omega DkT\kappa}. \quad (3.9.13)$$

The equations determining $v_j(r)$ are obtained by eliminating G_{ji} from (3.4.4) by means of the corresponding terms from the Poisson equation, which yields

$$b_{\mu\mu}^{\lambda} D_{\lambda} \left(\Delta \Delta v_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta v_j + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta v_i \right. \\ \left. + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta \xi_i - \frac{2\pi}{DkT} \sum_i \frac{e_i \zeta(r)}{n_j (\omega_i + \omega_j)} \right) = 0$$

By a procedure analogous to that used in simplifying the equation for $u_j(r)$, we obtain

$$\Delta \Delta v_j - \frac{4\pi}{DkT} n e^2 \Delta v_j + \frac{2\pi}{DkT} n e e_j (\Delta v_1 - \Delta v_2) = \\ = \frac{e_j \kappa}{16 \omega DkT} (3 - \kappa r) e^{-\kappa r}$$

and as before, $\Delta v_1 = -\Delta v_2$. Then

$$\Delta \Delta v_j = \frac{e_j \kappa}{16 \omega DkT} (3 - \kappa r) e^{-\kappa r}. \quad (3.9.14)$$

The solution of (3.9.14) which satisfies the boundary conditions is

$$v_j(r) = \frac{-e_j}{16 \omega DkT} \left(\frac{r e^{-\kappa r}}{\kappa^2} + \frac{5 e^{-\kappa r}}{\kappa^3} + 8 \frac{e^{-\kappa r} - 1}{\kappa^4 r} \right) \\ = \frac{-e_j}{16 \omega DkT} Z(r).$$

The term in $\frac{\partial \psi'}{\partial q^m}$ corresponding to $v_j(r)$ is

$$b_{\mu\mu}^{\lambda} D^2{}_{\lambda m} v_j(r) = b_{\mu\mu}^m \frac{d v_j}{r dr} + b_{\mu\mu}^{\lambda} q^m q^{\lambda} \frac{d^2 v_j}{(r dr)^2}.$$

By expanding $Z(r)$ in a power series and differentiating,

$$\frac{d Z(r)}{r dr} = \sum_{n=0}^{\infty} \frac{(-\kappa)^{n-1} r^n (n-1)(n+1)(n+2)}{(n+3)!}$$

and

$$\frac{d^2 Z(r)}{(r dr)^2} = \sum_{n=0}^{\infty} \frac{(-\kappa)^{n+1} r^n}{n! (n+5)}.$$

Then in the limit,

$$(b_{\mu\mu}^{\lambda} D^2{}_{\lambda m} v_j(r))_{r=0} = -b_{\mu\mu}^m \frac{e_j}{48 \omega DkT \kappa}. \quad (3.9.15)$$

c) Calculation of Total Force.

Combining the results (3.9.13) and (3.9.15),

$$\left(\frac{\partial \psi_j'}{\partial q^m} \right)_{r=0} = -b_{\mu\mu}^m \frac{e_j}{120 \omega DkT \kappa}.$$

This result may now be substituted in (3.9.2), whence we obtain

$$F^*_z = - \sum_j n_j e_j \left(\frac{\partial \psi'_j}{\partial x} \right)_{r=0} = b^1_{\mu\mu} \frac{\kappa}{480 \pi \omega} = b^1_{\mu\mu} \eta^*,$$

which is (3.9.4) with the previous value (3.7.3) for the electrostatic viscosity

$$\eta^* = \kappa / 480 \pi \omega.$$

4. Conductance and Diffusion

4.1. Introduction.

We shall investigate the problem of ions migrating in a general homogeneous field of forces, that is, external forces $\mathbf{k}_1, \dots, \mathbf{k}_s$ (per ion) acting on ions of the species 1, . . . , s , respectively, and a balancing force

$$n_0 \mathbf{k}_0 = - \sum_{i=1}^s n_i \mathbf{k}_i \quad (4.1.1)$$

acting on the molecules of the solvent.

We shall show that this system of forces is equivalent to an arbitrary combination of a homogeneous electric field $\mathbf{E} = -\text{grad } \varphi$ and uniform concentration gradients $\text{grad } n_1, \dots, \text{grad } n_s$, subject to the restriction of electric neutrality

$$\sum_{i=1}^s e_i \text{grad } n_i \equiv \text{grad } \sum_i n_i e_i = \text{grad } 0 = 0. \quad (4.1.2)$$

According to thermodynamics, equilibrium could be maintained with this system of field and gradients by introducing further *forces*

$$-\mathbf{k}_0, -\mathbf{k}_1, \dots, -\mathbf{k}_s$$

of some other nature, whereby

$$\mathbf{k}_i = -\text{grad } \mu_i = -\text{grad } (\mu'_i + e_i \varphi). \quad (4.1.3)$$

Here μ'_i stands for the ordinary thermodynamic potential, and μ_i for the *total potential* of an ion or molecule (without the hypothetical forces $-\mathbf{k}_i$). Now it is safe to assume that the velocities due to different causes of migration may be superimposed; therefore, the velocities caused by the potential gradients $-\text{grad } \mu_i$, ($i = 0, 1, \dots, s$) must be the same as those caused by equal forces $\mathbf{k}_0, \mathbf{k}_1, \dots, \mathbf{k}_s$ (4.1.3), because either will balance the system of forces $-\mathbf{k}_0, -\mathbf{k}_1, \dots, -\mathbf{k}_s$. On the basis of the Gibbs-Duhem theorem

$$S \delta T - V \delta p + \sum_i n_i \delta \mu'_i = 0$$

(where S = entropy; V = volume; p = pressure), the forces given by (4.1.3) conform to the equilibrium condition (4.1.1), assuming constant temperature and pressure. It is also seen that the free choice of $(s-1)$ concentration

¹ A system of forces not balancing each other as indicated by (4.1.1) would have to be balanced by a pressure gradient in the liquid. On thermodynamic grounds, the resulting motion of the substances present would be the same if a force equivalent to the pressure gradient were distributed among the molecules and ions in proportion to their partial volumes.

gradients, ($\text{grad } n_i$ and $\text{grad } n_0$ being given by (4.1.2) and by the condition $\text{grad } p = 0$), and of an electric potential gradient is equivalent to the free choice of s forces $\mathbf{k}_1, \dots, \mathbf{k}_s$ (\mathbf{k}_0 being given by (4.1.1)). The separation of μ_i into two parts μ'_i and $e_i\varphi$ is possible according to molecular theory; but only the sum $\mu_i = \mu'_i + e_i\varphi$ enters into thermodynamic relations, and can be measured by corresponding experiments. For the purposes of thermodynamics, an arbitrary convention about the separation is of course admissible if self-consistent. We have shown above that potential gradients $-\text{grad } \mu_i$ will cause the same migration of ions as equal forces. The "forces" thus defined are evidently not affected by an admissible convention about the electrical contribution to the total potentials, and, conversely, we cannot expect to obtain information about the actual electrostatic potentials from diffusion experiments.

We shall now investigate the effect of interionic forces on the migration of ions. An isolated ion would move relatively to the surrounding solvent with the velocity

$$\mathbf{v}_i = \mathbf{k}_i / \rho_i = \mathbf{k}_i \omega_i \quad (4.1.4)$$

where ρ_i is its coefficient of friction, and this law will be approached for very dilute solutions. If we were dealing with molecules instead of ions, and the different kinds of molecules were nearly enough alike to form an ideal solution, then we might expect a law similar to (4.1.4) to hold for finite concentrations as well. In the case of an electrolyte, however, the Coulomb forces between the ions will cause deviations from random distribution in the form of ionic atmospheres, and for this reason, the ions will affect each other's motion.

There are two different effects to be considered, namely the direct transfer of electric forces between the ions and a hydrodynamic effect, the so-called electrophoresis. The latter effect was recognized by Debye and Hückel, while the former had been expected for a long time by those familiar with the properties of electrolytes.

We can get an idea about the force effect and estimate its order of magnitude if we consider one particular ion moving under the action of a force \mathbf{k} . Its velocity will be (nearly)

$$\mathbf{v} = \mathbf{k} / \rho.$$

When the ion starts moving, at first its atmosphere will be left behind; but the displaced ion will soon exert an electric pull on its lagging atmosphere, which will continue to form around the ion as it moves along and to scatter in the rear. The ion will maintain a lead of the order τ seconds, where τ is the relaxation time, (1.3.4) of the atmosphere, corresponding to a distance

$$v\tau = \mathbf{k}\tau / \rho.$$

The ratio of this distance to the radius $1/\kappa$ of the ionic atmosphere gives the relative dissymmetry of the latter,

$$\kappa \mathbf{k} \tau / \rho;$$

thus the directed component $\Delta \mathbf{k}$ of the total force $e^2 \kappa / D$ between ion and atmosphere will be of the order

$$-(e^2\kappa^2/D)\kappa\mathbf{k}\tau/\rho = -\kappa\tau e^2\kappa^3/\rho D$$

retarding the ion. Substituting (1.3.4) for the time of relaxation, we obtain

$$\Delta\mathbf{k} \approx -e^2\kappa\mathbf{k}/DkT = -\kappa d_0\mathbf{k} \quad (4.1.5)$$

(cf. 1.3.3), which indeed agrees with the results to be derived in the following, except for a numerical factor.

By the principle of action and reaction, the force (4.1.5) is taken up by the ions in the atmosphere and, conversely, if some of the ions in the atmosphere are caused to migrate under the influence of external forces, "blowing" part of the structure to one side, the central ion will receive a force on account of the resulting asymmetry. We might also consider the central ion, as forming part of the other ions' atmospheres; the relation of neighborhood is a reciprocal one. In order to make this reciprocity complete, it is necessary to consider the Brownian motion of the central ion, which thereby contributes to the relaxation of its own atmosphere; in our fundamental equations (2.5.7), due allowance has been given for this effect.

The *electrophoresis* is most simply described and estimated for the case of electrical conduction where, for an electric field \mathbf{E} ,

$$\mathbf{k}_0 = 0; \mathbf{k}_i = e_i\mathbf{E}. \quad (i = 1, \dots, s)$$

The atmosphere of an ion of charge e_j will contain the total electric charge $-e_j$ and consequently be subject to a total force $-\mathbf{E}e_j$ in the field \mathbf{E} . This force will be taken up by the liquid in which the ions of the atmosphere are embedded, and cause hydrodynamic motion in the direction of the force $-\mathbf{E}e_j$. For an estimate of the effect, we may assume the entire charge $-e_j$ of the atmosphere situated at a distance equal to the mean radius $1/\kappa$, uniformly distributed on a spherical shell. Then according to Stokes' law, the interior of the sphere will move with the velocity

$$\Delta\mathbf{v}_j = -\mathbf{E}e_j/6\pi\eta\kappa^{-1} = -\mathbf{E}e_j\kappa/6\pi\eta \quad (4.1.6)$$

where η = viscosity. The liquid that immediately surrounds the central ion will be moving with the velocity $\Delta\mathbf{v}_j$, and this ion, as it migrates in the electric field, must swim in a countercurrent of the magnitude (4.1.6). If the ion had no atmosphere, it would move with the velocity

$$\mathbf{k}_j/\rho_j = \mathbf{E}e_j/\rho_j.$$

Surrounded by an atmosphere, the ion is subject to a force $\mathbf{k}_j - \Delta\mathbf{k}_j$ (on account of the correction (4.1.5)); but the velocity corresponding to this force, namely

$$(\mathbf{k}_j - \Delta\mathbf{k}_j)/\rho_j,$$

describes the motion relative to a neighborhood moving with the velocity $\Delta\mathbf{v}_j$, so that the net velocity will be

$$\mathbf{v}_j = \Delta\mathbf{v}_j + (\mathbf{k}_j - \Delta\mathbf{k}_j)/\rho_j \quad (4.1.7)$$

or in the particular case of electric conduction

$$\mathbf{v}_j = \frac{\mathbf{E}e_j - \Delta\mathbf{k}}{\rho_j} - \frac{\mathbf{E}e_j\kappa}{6\pi\eta}.$$

Incidentally, the formula (4.1.6) gives an exact value for the electrophoretic effect, except for possible refinements, (not affecting the limiting \sqrt{c} formula), applied to the assumed value for the radius of the ionic atmosphere. In the general case of arbitrary forces $\mathbf{k}_0, \mathbf{k}_1, \dots, \mathbf{k}_s$, there will also be an electrophoretic effect, because the concentrations in the ionic atmosphere differ from the average concentrations n_1, \dots, n_s in the bulk of the solution, so that the force balance (4.1.1) is upset, and the resulting force density in the atmosphere will cause hydrodynamic motion.

According to (4.1.5) and (4.1.6), both the force effect and the electrophoresis are proportional to the square root of the concentration, on account of the factor $\kappa \sim \sqrt{c}$. The two effects are ordinarily of the same order of magnitude; they change the velocity of an ion of radius b by amounts of the order

$$\kappa d_0 \mathbf{k} / \rho = \mathbf{k} \kappa d_0 / 6\pi\eta b$$

and

$$\mathbf{k} \kappa / 6\pi\eta$$

respectively, and we have already pointed out that according to (1.3.3), $d_0 = e^2/DkT$ is comparable to the radius b of an ordinary ion. For KCl in water at 25°C. and 0.001*n* concentration, the force effect is 0.75%, the electrophoresis 1.26% of the limiting equivalent conductance.

4.2. *Electrophoresis.*

In this section, we shall review briefly a previous calculation¹ of the decrease in velocity of an ion due to electrophoresis, and extend the treatment to deal with the general problem of ionic migration. In the case of electrolytic conduction, a given ion does not move with respect to a medium at rest, but, since it is surrounded by an atmosphere of ions which move in the opposite direction, it actually travels with respect to a moving medium. If the applied force on a j -ion is \mathbf{k}_j , then, as pointed out in the previous paragraph, instead of using the velocity

$$\mathbf{v}_j = \mathbf{k}_j \omega_j$$

to compute transfer of ions (and charge), we must use $\mathbf{v}_j - \Delta\mathbf{v}_j$, where $\Delta\mathbf{v}_j$ is the so-called electrophoretic correction.

The electrophoretic effect is due to a volume force attacking in the liquid that surrounds an ion. If the average concentration of j -ions is n_j , the average applied force on the ions contained in a unit volume of solution is

$$\sum_{j=1}^s n_j \mathbf{k}_j = n_\sigma \mathbf{k}_\sigma$$

This force is transferred to the n_σ solvent molecules per unit volume of solution; the equilibrium condition (4.1.1) may be written symmetrically

$$n_\sigma \mathbf{k}_\sigma + n_0 \mathbf{k}_0 = 0. \quad (4.2.1)$$

But the force acting on the ions in an element of volume dV near a j -ion is $n_{j\sigma} \mathbf{k}_\sigma dV$ because the presence of a j -ion changes the average concentrations in

¹ L. Onsager: *Physik. Z.*, 27, 388 (1926).

dV by electrostatic interaction; the force on the solvent remains $n_o \mathbf{k}_o dV$. Therefore there acts on dV a net force equal to

$$(n_{j\sigma} \mathbf{k}_\sigma + n_o \mathbf{k}_o) dV = (n_{j\sigma} - n_\sigma) \mathbf{k}_\sigma dV. \quad (4.2.2)$$

In calculating the electrophoresis, we shall neglect the asymmetry of the ionic atmospheres.¹

In spherical coordinates (with the j -ion at the origin), $dV = r^2 dr d\Omega$ so that the force acting on a spherical shell of solution at a distance r from the central ion is

$$4\pi r^2 (n_{j\sigma} - n_\sigma) \mathbf{k}_\sigma dr. \quad (4.2.3)$$

This force is uniformly distributed over the shell and is in the direction of the applied force \mathbf{k} . This distribution of forces is the same as that acting on a solid sphere of radius r moving through a liquid of viscosity η . We therefore may apply Stokes' formula

$$\mathbf{V} = \mathbf{P}/6\pi\eta r. \quad (4.2.4)$$

A force \mathbf{P} , applied as described, will cause all the points in the interior of the spherical shell to move with the *same* velocity \mathbf{V} .

In order to calculate the force density, we must first obtain $(n_{ji} - n_i)$ as a function of r . According to the Boltzmann distribution (and our definition of n_{ji} and ψ_i ,

$$n_{ji} = n_i \exp(-e_i \psi_j^o / kT). \quad (4.2.5)$$

In approximating the exponential by its series expansion, we shall retain the term involving e_i^2 , because the contribution of the e_i term to diffusion flow will depend on (the square of) the difference of the mobilities of the ions present. To this approximation

$$n_{ji} \approx n_i \left\{ 1 - \frac{e_i \psi_j^o}{kT} + \frac{1}{2} \left(\frac{e_i \psi_j^o}{kT} \right)^2 \right\}. \quad (4.2.6)$$

For the potentials, we shall use Debye's second approximation²

$$\psi_j^o = \frac{e_j}{D} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r} \quad (4.2.7)$$

where a is the distance at which the atmosphere of the ion begins. Substituting (4.2.7) in (4.2.6), and the result in (4.2.3), we obtain for the force acting on a spherical shell around the j -ion

¹ Tentative calculations have shown that this approximation will not affect the limiting law for small concentrations and that the terms thus neglected (of the order $c \log c$) are in general of minor importance. In the case of diffusion, these terms vanish in the absence of a diffusion-potential, like the first (\sqrt{c}) terms in (4.2.14) and may be considered as corrections to the latter.

² It may appear inconsequent to retain the e^2 term in (4.2.6) and drop the corresponding term in the approximation (4.2.7) for the potential. We have, however, carried through the derivation using the next approximation for the potential given by LaMer and Mason: J. Am. Chem. Soc., 49, 420 (1927), and the final result differs from the one obtained here only by a term of the order of concentration to the first power. Furthermore, it has a small numerical coefficient, and vanishes for a symmetrical electrolyte.

$$\begin{aligned} \mathbf{F} dr &= 4\pi r^2 \left\{ \frac{-e_j e_\sigma}{D k T} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r} + \frac{1}{2} \left(\frac{e_j e_\sigma}{D k T} \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-2\kappa r}}{r^2} \right\} n_\sigma \mathbf{k}_\sigma dr \\ &= 4\pi (-A_1 r e^{-\kappa r} + A_2 e^{-2\kappa r}) dr. \end{aligned}$$

If we now apply Stokes' formula (4.2.4), this force is seen to give a velocity

$$d\mathbf{v}_j = \frac{\mathbf{F} dr}{6\pi\eta r} = \frac{2}{3\eta} \left(-A_1 e^{-\kappa r} + A_2 \frac{e^{-2\kappa r}}{r} \right) dr \quad (4.2.8)$$

to the shell and the ion at its centre. In order to obtain the total velocity produced by the entire atmosphere of the ion, we simply integrate (4.2.8), whence

$$\begin{aligned} \Delta\mathbf{v}_j &= \frac{2}{3\eta} \int_a^\infty \left\{ -A_1 e^{-\kappa r} + A_2 \frac{e^{-2\kappa r}}{r} \right\} dr \\ &= \frac{2}{3\eta} \left\{ -A_1 \frac{e^{-\kappa a}}{\kappa} + A_2 \text{Ei}(2\kappa a) \right\} \end{aligned} \quad (4.2.9)$$

where $\text{Ei}(x)$ is the exponential integral function

$$\text{Ei}(x) = \int_x^\infty e^{-t} \frac{dt}{t} = -0.5772 - \log x + x - \frac{x^2}{2 \cdot 2!} + \dots$$

If we replace the constants of (4.2.9), we obtain the electrophoretic correction to the velocity

$$\Delta\mathbf{v}_j = -\frac{2}{3\eta} \frac{e_j e_\sigma n_\sigma \mathbf{k}_\sigma}{D k T \kappa (1 + \kappa a)} + \frac{1}{3\eta} \left(\frac{e_j e_\sigma}{D k T} \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 n_\sigma \mathbf{k}_\sigma \text{Ei}(2\kappa a). \quad (4.2.10)$$

For an electrical force $\mathbf{k}_i = \mathbf{E} e_i$, and κa small, the first term becomes

$$-\mathbf{E} e_j \kappa / 6\pi\eta \quad (4.2.11)$$

which is Onsager's result.

Next, we shall see how the electrophoretic correction (4.2.10) affects the diffusion of a simple electrolyte ($s=2$) where $\mathbf{k}_j = \mathbf{v}/\omega_j$, if \mathbf{v} is the net velocity of diffusion. The velocity correction becomes

$$\begin{aligned} \Delta\mathbf{v}_j &= -\frac{2}{3\eta} \left(\frac{n_1 e_1}{\omega_1} + \frac{n_2 e_2}{\omega_2} \right) \frac{e_j \mathbf{v}}{D k T \kappa (1 + \kappa a)} + \\ &\quad \frac{1}{3\eta} \left(\frac{n_1 e_1^2}{\omega_1} + \frac{n_2 e_2^2}{\omega_2} \right) \frac{\mathbf{v} e_j^2}{(D k T)^2} \varphi(\kappa a) \end{aligned} \quad (4.2.12)$$

where

$$\varphi(\kappa a) = e^{2\kappa a} \text{Ei}(2\kappa a) / (1 + \kappa a)^2.$$

The corresponding force is, per unit volume

$$\sum_j n_j \Delta\mathbf{v}_j / \omega_j.$$

To evaluate this sum, we substitute (4.2.12), carry out the summation and use the following relations

$$n_1 e_1 + n_2 e_2 = 0 \quad (4.2.13a)$$

$$\bar{\rho} = \frac{n_1 e_1^2 / \omega_1 + n_2 e_2^2 / \omega_2}{n_1 e_1^2 + n_2 e_2^2} \quad (4.2.13b)$$

$$\kappa^2 = \frac{4\pi}{DkT} (n_1 e_1^2 + n_2 e_2^2). \quad (4.2.13c)$$

Then

$$\sum_j n_j \Delta \mathbf{v}_j / \omega_j = - \frac{\mathbf{v}}{6\pi\eta} \frac{n_1 n_2}{n_1 + n_2} \frac{\kappa}{1 + \kappa a} (\rho_1 - \rho_2)^2 + \frac{(\bar{\rho})^2 \mathbf{v} \kappa^4}{48\pi^2 \eta} \varphi(\kappa a).$$

The average force per ion is accordingly

$$\frac{\sum_j n_j \Delta \mathbf{v}_j / \omega_j}{n_1 + n_2} = \mathbf{v} \left(\frac{-1}{6\pi\eta (z_1 + z_2)^2} \frac{\kappa}{(1 + \kappa a)} (\rho_1 - \rho_2)^2 + \frac{(\bar{\rho})^2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta (n_1 + n_2)} \right) \quad (4.2.14)$$

where we have introduced the valences $z_1 = |e_1|/\epsilon$ and $z_2 = |e_2|/\epsilon$ in the first term. The correction is, first of all, proportional to the velocity, (i.e. to the acting force, which in the case of diffusion is the gradient of the total chemical potential μ . This point will be discussed in detail in §4.13). The two terms of (4.2.14) are of opposite sign. The first term depends on the square root of the concentration and on the square of the *difference* in mobility of the two ions present. The second term is of the order $c \log c$ (c = concentration) and otherwise depends only on the average (with respect to ionic strength) of the mobilities.

We shall need for a later discussion the contribution to diffusion due to electrophoresis. The corresponding number of ions per second crossing a unit area perpendicular to the direction of diffusion equals

$$\begin{aligned} \Delta J_j &= n_j \Delta \mathbf{v}_j = \\ &= \left(- \frac{2}{3\eta} \frac{n_j e_j n_\sigma e_\sigma}{DkT \kappa(1 + \kappa a)} + \frac{1}{3\eta} \frac{n_\sigma e_\sigma^2 n_j e_j^2 \varphi(\kappa a)}{(DkT)^2} \right) \mathbf{k}_\sigma. \end{aligned} \quad (4.2.15)$$

If we write $\Delta J_j = \Delta \Omega_{j\sigma} \mathbf{k}_\sigma$, then

$$\begin{aligned} \Delta \Omega_{ji} &= \frac{\partial \Delta J_j}{\partial \mathbf{k}_i} = \\ &= - \frac{2}{3\eta} \frac{n_j e_j n_i e_i}{DkT \kappa(1 + \kappa a)} + \frac{1}{3\eta} \frac{n_i e_i^2 n_j e_j^2 \varphi(\kappa a)}{(DkT)^2}. \end{aligned} \quad (4.2.16)$$

This result applies to an arbitrary mixture of ions. We note that $\Delta \Omega_{ji}$ is symmetrical as required (cf. §4.15).

For a simple electrolyte, we have, using (4.2.13),

$$\Delta\Omega_{11} = -\frac{n_1 z_1 \kappa}{6\pi\eta (1 + \kappa a) (z_1 + z_2)} + \frac{z_1^2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta (z_1 + z_2)^2} \quad (4.2.17a)$$

$$\Delta\Omega_{12} = \frac{n_1 z_1 \kappa}{6\pi\eta (1 + \kappa a) (z_1 + z_2)} + \frac{z_1 z_2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta (z_1 + z_2)^2} = \Delta\Omega_{21} \quad (4.2.17b)$$

$$\Delta\Omega_{22} = -\frac{n_1 z_1 \kappa}{6\pi\eta (1 + \kappa a) (z_1 + z_2)} + \frac{z_2^2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta (z_2 + z_2)^2} \quad (4.2.17c)$$

4.3. Specialization of the Fundamental Equations for Ionic Forces.

In adapting the general equation of continuity (2.5.7) to the conductance diffusion problem, we naturally consider the special case where no velocity gradient is present. Accordingly, the velocity terms drop out and furthermore, ψ'_j and f_{ji} no longer depend on location, so that we simply have to deal with functions of the form $\psi'_j(\mathbf{r}_{21})$. Then (2.5.7) becomes

$$\begin{aligned} & \omega_i(\mathbf{K}_i, \text{grad}_2 f_{ji}^\circ(r)) + \omega_j(\mathbf{K}_j, \text{grad}_1 f_{ij}^\circ(r)) \\ & - e_i \omega_i n_i n_j \Delta_2 \psi'_j(\mathbf{r}_{21}) - e_j \omega_j n_i n_j \Delta_1 \psi'_i(-\mathbf{r}_{21}) \\ & - \omega_i k T \Delta_2 f'_{ji}(\mathbf{r}_{21}) - \omega_j k T \Delta_1 f'_{ij}(-\mathbf{r}_{21}) = 0. \end{aligned} \quad (4.3.1)$$

The differential operators in the above equation may all be reduced to differentiation with respect to $q^l = q_{21}^l$ ($l = 1, 2$, and 3) since there are no longer functions of \mathbf{r}_1 or \mathbf{r}_2 present. Since $q_{21} = q_2 - q_1$ and $f_{ji}^\circ(r) = f_{ij}^\circ(r)$, we have

$$\text{grad}_1 f_{ij}^\circ(r) = -\text{grad}_2 f_{ij}^\circ(r) = -\text{grad} f_{ji}^\circ(r)$$

and

$$\Delta_2 = \Delta_1 = \Delta_{21} = \Delta.$$

If we now write \mathbf{r} for \mathbf{r}_{21} and $-\mathbf{r}$ for \mathbf{r}_{12} , the subscripts 1, 2 may be dropped and we obtain

$$\begin{aligned} & \omega_i(\mathbf{K}_i, \text{grad} f_{ji}^\circ(r)) - \omega_j(\mathbf{K}_j, \text{grad} f_{ji}^\circ(r)) \\ & - e_i \omega_i n_i n_j \Delta \psi'_j(\mathbf{r}) - e_j \omega_j n_i n_j \Delta \psi'_i(-\mathbf{r}) \\ & - \omega_i k T \Delta f'_{ji}(\mathbf{r}) - \omega_j k T \Delta f'_{ij}(-\mathbf{r}) = 0. \end{aligned} \quad (4.3.2)$$

We defined ψ'_j and f'_{ji} in §2.5 as the asymmetric additions to potential and distribution produced by any agency which destroyed the symmetry of the ionic atmospheres. They were assumed small with respect to the functions ψ°_j and f_{ji}° characteristic of the solution in the unperturbed state. Now here we shall consider the effects due to a force \mathbf{k} and shall assume ψ'_j and f'_{ji} proportional to this force. For the migration problem this means, then, that we limit the discussion to conductance and diffusion under ordinary field strengths and concentration gradients, where proportionality applies.¹ Consequently, the general form of the addition functions must be

$$(\mathbf{r}, \mathbf{k}) R(r) \quad (4.3.3)$$

¹ Arguments based on this limitation were first used in connection with the Debye-Hückel theory by Redlich: *Physik. Z.*, **26**, 199 (1925).

where $R(r)$ is a function of the scalar distance r and where (\mathbf{r}, \mathbf{k}) , linear in \mathbf{k} as required, gives the dependence on direction. Functions of this type must satisfy the following symmetry conditions

$$\varphi(-\mathbf{r}) = -\varphi(\mathbf{r}), \text{ i.e.,}$$

$$\psi'_i(-\mathbf{r}) = -\psi'_i(\mathbf{r})$$

$$f'_{ji}(-\mathbf{r}) = -f'_{ji}(\mathbf{r}) = -f'_{ij}(-\mathbf{r}); f'_{ji} = 0. \quad (4.3.4)$$

If we substitute these in (4.3.2) and recall that $f'_{ij}(-\mathbf{r}) = f'_{ji}(\mathbf{r})$, the resulting equation will contain only functions of \mathbf{r} :

$$\begin{aligned} \omega_i(\mathbf{k}_i, \text{grad } f^\circ_{ji}) - \omega_j(\mathbf{k}_j, \text{grad } f^\circ_{ji}) - e_i \omega_i n_i n_j \Delta \psi'_j(\mathbf{r}) \\ + e_j \omega_j n_i n_j \Delta \psi'_i(\mathbf{r}) - (\omega_i + \omega_j) kT \Delta f'_{ji}(\mathbf{r}) = 0. \end{aligned} \quad (4.3.5)$$

This may be simplified further with no actual loss of generality by the assumption that the forces $\mathbf{k}_i, \mathbf{k}_j$ have components k_i, k_j only in the x -direction; then

$$(\mathbf{k}, \text{grad } f^\circ_{ji}) = k \frac{\partial f^\circ_{ji}}{\partial x}$$

and (4.3.5) becomes

$$\begin{aligned} (\omega_i k_i - \omega_j k_j) \frac{\partial f^\circ_{ji}}{\partial x} - e_i \omega_i n_i n_j \Delta \psi'_j + \\ e_j \omega_j n_i n_j \Delta \psi'_i - (\omega_i + \omega_j) kT \Delta f'_{ji} = 0. \end{aligned} \quad (4.3.6)$$

In view of the relations (4.3.4), there are $\frac{1}{2} s(s-1)$ independent distribution functions f'_{ji} ; (4.3.6) accordingly is a system of $\frac{1}{2} s(s-1)$ differential equations connecting these with the s potentials.

4.4. Differential Equations for the Potentials.

By means of the s Poisson equations

$$\Delta \psi'_j = -\frac{4\pi}{D} \sum_i \frac{e_i}{n_i} f'_{ji} \quad (4.4.1)$$

the system (4.3.6) is made complete, and we may now eliminate the distribution functions from (4.3.6) by means of (4.4.1)

$$\begin{aligned} \Delta \Delta \psi'_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta \psi'_j + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta \psi'_i = \\ = -\frac{4\pi}{DkT} \sum_i \frac{\omega_i k_i - \omega_j k_j}{\omega_i + \omega_j} \frac{e_i}{n_j} \frac{\partial f^\circ_{ji}}{\partial x} \\ = \frac{4\pi}{(DkT)^2} \sum_i \frac{\omega_i k_i - \omega_j k_j}{\omega_i + \omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{r} \right) \end{aligned} \quad (4.4.2)$$

on substituting the value of f°_{ji} given by (2.4.11).

It has been pointed out previously¹ that by multiplying (4.4.2) by $n_j e_j$ and summing over j that

$$\sum_j n_j e_j \Delta \psi'_j = 0, \quad (4.4.3)$$

and since ψ'_j and $\Delta \psi'_j$ must vanish for $r = \infty$ and always remain finite,

$$\sum_i n_i e_i \Delta \psi'_i = 0.$$

If we write i for j in the last equation and multiply by $4\pi e_i/DkT$, we obtain

$$\frac{4\pi}{DkT} \sum_i n_i e_i e_j \Delta \psi'_i = 0$$

which may be subtracted from (4.4.2). From the resulting set of coefficients, when we later introduce matrix formulation, we shall obtain the same symmetrical matrix K that appeared in the viscosity problem. We shall then be able to utilize our knowledge of the properties of K in our present problem. After subtraction, we have

$$\begin{aligned} \Delta \psi'_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta \psi'_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j} \Delta \psi'_i = \\ = \frac{4\pi}{(DkT)^2} \sum_i \frac{\omega_i k_i - \omega_j k_j}{\omega_i + \omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x} \left(\frac{e^{-rk}}{r} \right) \end{aligned} \quad (4.4.4)$$

as the differential equations determining the potentials ψ'_j .

4.5. Matrix Formulation and Solution.

The equations (4.4.4) can be written compactly by introducing matrix notation and s -dimensional vectors in "ion-space." Again we shall find that in this form, the equations are readily solved explicitly for the general case of s ions. Let the elements of a matrix C be defined by

$$c_{ji} = \frac{4\pi}{DkT} \left(\frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_\sigma + \omega_j} \delta_{ji} + \frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j} \right) \quad (4.5.1)$$

and the components h_j of a vector \mathbf{h} by

$$h_j = \frac{4\pi}{(DkT)^2} \left(\frac{k_\sigma \omega_\sigma - k_j \omega_j}{\omega_\sigma + \omega_j} n_\sigma e_\sigma^2 e_j \right). \quad (4.5.2)$$

(Greek indices always imply summation over $\sigma = 1, 2, \dots, s$). Then we may write (4.4.4) as

$$\Delta (\Delta \delta_{j\tau} - c_{j\tau}) \psi'_\tau = h_j \frac{\partial}{\partial x} \left(\frac{e^{-kr}}{r} \right)$$

which is the component form of the operator equation

$$\Delta (\Delta - C) \mathbf{y} = \mathbf{h} \frac{\partial}{\partial x} \left(\frac{e^{-kr}}{r} \right) \quad (4.5.3)$$

if \mathbf{y} is a vector with components ψ'_j .

¹ Onsager: Loc. cit., p. 284.

The matrix C is made symmetrical by the following transformation:

$$\begin{aligned} K &= P C P^{-1} \\ p_{ji} &= \delta_{ji} \sqrt{n_j \omega_j} \\ k_{ji} &= \frac{4\pi}{DkT} \left(\frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_\sigma + \omega_j} \delta_{ji} + \frac{e_i e_j \sqrt{n_i n_j \omega_i \omega_j}}{\omega_i + \omega_j} \right) \end{aligned} \quad (4.5.4)$$

The result K of this transformation is the same matrix K that appeared in the viscosity problem. We have shown that its characteristic numbers $\alpha_1, \dots, \alpha_s$ are all positive (3.8.4) and that $\alpha_1 = \kappa^2$ (3.8.6) is the greatest of them. Also the eigenvector l_1 corresponding to α_1 is given by (3.8.5)

$$l_{1j} = e_j \sqrt{n_j / \omega_j} (n_\sigma e_\sigma^2 / \omega_\sigma)^{-1/2}. \quad (4.5.5)$$

Since, by (4.5.1), the matrix C has the same characteristic numbers as K , all real ≥ 0 ; the matrices G satisfying

$$G^2 = C, \quad g_{j\sigma} g_{\sigma i} = c_{ji}, \quad (4.5.6)$$

will all be real. One of these will have all characteristic numbers $\sqrt{\alpha_1}, \dots, \sqrt{\alpha_s}$ positive: we shall represent this particular one simply by G .

Now if $\varphi(r, \gamma)$ is a solution of

$$\Delta (\Delta - \gamma^2) \varphi(r, \gamma) = \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{r} \right), \quad (4.5.7)$$

then in accordance with the definitions of functions of matrices,¹

$$\Delta (\Delta - G^2) \varphi(r, G) = \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{r} \right) \mathbf{1} \quad (4.5.8)$$

so that $\Delta (\Delta - G^2) \varphi(r, G)$ operating on \mathbf{h} is the same as multiplying \mathbf{h} by the scalar function $\frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{r} \right)$. Then

$$\mathbf{y} = \varphi(r, G) \mathbf{h} \quad (4.5.9)$$

is a solution of (4.5.3).

We now proceed to find the solution of (4.5.7) which satisfies the boundary conditions that the potential must vanish for $r = \infty$ and must remain finite for all values of r . (The boundary conditions for potentials have been discussed in detail in a preceding section, §3.5.) A particular solution of (4.5.7) is

$$\varphi(r, \gamma) = \frac{1}{\kappa^2(\kappa^2 - \gamma^2)} \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{r} \right),$$

to which we add the general solution of the homogeneous equation. According to (4.3.3), we only have to consider functions of the type $xR(r)$, or what amount to the same, of the form $\partial R(r)/\partial x$. With this restriction, the most general solution of (4.5.7) is

$$\varphi(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2} \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{\kappa^2 r} + A_1 \frac{e^{\gamma r}}{r} + A_2 \frac{e^{-\gamma r}}{r} + A_3 r^2 + A_4 \frac{1}{r} \right).$$

¹ See also footnote following (3.5.7a).

In order that φ vanish for $r = \infty$,

$$A_1 = A_3 = 0,$$

and in order that $\Delta\varphi$ remain finite at $r = 0$,

$$A_2 = -1/\gamma^2.$$

Then, on substituting these constants, we see that

$$A_4 = \frac{1}{\gamma^2} - \frac{1}{\kappa^2}$$

in order that φ remain finite at $r = 0$. Our solution is accordingly

$$\varphi(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2} \frac{\partial}{\partial x} \left(\frac{1 - e^{-\gamma r}}{\gamma^2 r} - \frac{1 - e^{-\kappa r}}{\kappa^2 r} \right). \quad (4.5.10)$$

We are now able to write the solution of the matrix equation (4.5.3)

$$\mathbf{y} = \varphi(r, \mathbf{G}) \mathbf{h}$$

$$\psi'_j = \varphi(r, G)_{j\sigma} h_\sigma \quad (4.5.11)$$

which satisfies the boundary conditions of the problem since G has all characteristic numbers positive. We also assert that this solution is unique; for proof, we refer to the entirely parallel case in §3.5.

In the conductance-diffusion problem, we shall be particularly interested in the value of the field strength $-\text{grad } \psi'_j$ for $r = 0$. By expanding the exponentials in power series and carrying out the differentiation with respect to x indicated in (4.5.10), we obtain

$$\varphi(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2} \left(\frac{\gamma - \kappa}{3} x + \frac{\kappa^2 - \gamma^2}{8} rx + O(r^2) \right)$$

and

$$\frac{\partial \varphi(r, \gamma)}{\partial x} = \frac{1}{\kappa^2 - \gamma^2} \left(\frac{\gamma - \kappa}{3} + \frac{\kappa^2 - \gamma^2}{8} r + \frac{\kappa^2 - \gamma^2}{8} \frac{x^2}{r} + O(r^2) \right).$$

In the limit $r = 0$ this becomes

$$\left(\frac{\partial \varphi}{\partial x} \right)_{r=0} = -\frac{1}{3} (\kappa + \gamma)^{-1}$$

so that

$$\text{grad}_x \psi'_j(0) = -\frac{1}{3} \{ (\kappa + G)^{-1} \}_{j\sigma} h_\sigma. \quad (4.5.12)$$

4.6. Simplification of Matrix Solution.

The rather complicated ion-vector \mathbf{h} can now be simplified if we write

$$h_j = \frac{1}{DkT} b_{j\sigma} k_\sigma \quad (4.6.1)$$

and identify by comparison with (4.5.2) the elements b_{ji} to be

$$b_{ji} = \frac{4\pi}{DkT} \left(\frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} e_j - \delta_{ji} \frac{n_\sigma e_\sigma^2 \omega_j}{\omega_j + \omega_\sigma} e_j \right).$$

In the last term we may write either i or j as subscript, due to the coefficient δ_{ji} ; then

$$\begin{aligned} b_{ji} &= \frac{4\pi}{DkT} \left(\frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j} + \delta_{ji} \frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_j + \omega_\sigma} - \delta_{ji} n_\sigma e_\sigma^2 \right) e_i \\ &= (c_{ji} - \delta_{ji} \kappa^2) e_i. \end{aligned} \quad (4.6.2)$$

Substituting this value in (4.6.1),

$$h_j = \frac{1}{DkT} (C - \kappa^2)_{j\sigma} e_\sigma k_\sigma$$

or

$$\mathbf{h} = \frac{1}{DkT} (\mathbf{C} - \kappa^2) \mathbf{m}, \quad (4.6.3)$$

where \mathbf{m} is a vector with components $e_j k_j$. The value of $\text{grad}_x \psi'_j(\mathbf{o})$ given by (4.5.12) now becomes

$$\begin{aligned} \text{grad}_x \psi'_j(\mathbf{o}) &= \frac{1}{3 DkT} \{ (\kappa + C^{1/2})^{-1} \}_{j\tau} (\kappa^2 - C)_{\tau\sigma} e_\sigma k_\sigma \\ &= \frac{1}{3 DkT} (\kappa - C^{1/2})_{j\sigma} e_\sigma k_\sigma \\ &= \frac{1}{3 DkT} \frac{\kappa}{\sqrt{n_j \omega_j}} (1 - \kappa^{-1} K^{1/2})_{j\sigma} \sqrt{n_\sigma \omega_\sigma} e_\sigma k_\sigma. \end{aligned} \quad (4.6.4)$$

This result for the field strength produced by the asymmetry of the ionic atmosphere involves the root $G = C^{1/2}$ of the matrix C . There are several ways in which the numerical computation may be made. One method, which is always applicable and in most cases convenient, proceeds by expansion of the function $f(K) = (1 - \kappa^{-1} K^{1/2})$ in a Taylor series. The series obtained will ordinarily converge rapidly except for the terms in the sum corresponding to the maximum characteristic number $\alpha_1 = \kappa^2$. This inconvenient behavior of the series may be correct by any one of several devices; we prefer to use the same one which served in the viscosity problem.

We have explicitly the eigenvector \mathbf{l}_1 (4.5.5). An eigenvector \mathbf{l}_j corresponding to a characteristic number α_j of a matrix \mathbf{A} is by definition a vector such that

$$\mathbf{A} \mathbf{l}_j = \alpha_j \mathbf{l}_j,$$

i.e., operating on \mathbf{l}_j with the tensor \mathbf{A} is equivalent to multiplying by the scalar α_j . Consequently $(f(\mathbf{C}), \mathbf{l}_1)$ vanishes, and we may add to the vector \mathbf{t} in (4.6.4) with the components $t_i = e_i k_i \sqrt{n_i \omega_i}$ any multiple of \mathbf{l}_1 , without changing the value of the product. The component of \mathbf{t} "parallel" to \mathbf{l}_1 is given by

$$(\mathbf{l}_1, \mathbf{t}) \mathbf{l}_1 = e_j \sqrt{\frac{n_j}{\omega_j}} \frac{n_\sigma e_\sigma^2 k_\sigma}{n_\tau e_\tau^2 / \omega_\tau}$$

and the component "perpendicular" to l_1 is then given by

$$t_i - (l_1, t) l_{1i} = \sqrt{n_i \omega_i} e_i k_i - \sqrt{\frac{n_i}{\omega_i} \frac{n_\sigma e_\sigma^2 k_\sigma}{n_\tau e_\tau^2 \rho_\tau}} e_i = p_i. \quad (4.6.5)$$

The vector \mathbf{p} thus determined may then replace \mathbf{t} in (4.6.4); but by construction, \mathbf{p} is orthogonal to l_1 , so that the terms corresponding to $\alpha_1 = \kappa^2$ will never appear when the sum is computed. With this substitution, (4.6.4) becomes

$$\text{grad}_x \psi'_j(\mathbf{o}) = \frac{\kappa}{3 DkT} \frac{1}{\sqrt{n_j \omega_j}} (1 - \kappa^{-1} K^{1/2})_{j\sigma} p_\sigma. \quad (4.6.6)$$

The series expansion is readily obtained by considering $f(z) = 1 - \sqrt{z}$. By substituting $z = t + 1/2$, we have the following identities:

$$\begin{aligned} 1 - \sqrt{z} &= (\sqrt{2} - \sqrt{1+2t}) 2^{-1/2} \\ (1+2t)^{1/2} &= \sum_{n=0}^{\infty} \binom{1/2}{n} (2t)^n \\ 1 - \sqrt{z} &= 2^{-1/2} \left\{ \sqrt{2} - \sum_{n=0}^{\infty} \binom{1/2}{n} (2t)^n \right\} \\ &= \sum_{n=0}^{\infty} c_n (2z - 1)^n \end{aligned} \quad (4.6.7)$$

where

$$c_0 = \frac{1}{2} (2 - \sqrt{2}); c_n = -\frac{\sqrt{2}}{2} \binom{1/2}{n} \text{ for } n \geq 1. \quad (4.6.8)$$

$$\begin{array}{ll} c_0 = 0.2929 & c_3 = -0.0442 \\ c_1 = -0.3536 & c_4 = 0.0276 \\ c_2 = 0.0884 & c_5 = -0.0193 \end{array}$$

Then

$$f(\mathbf{K}) \mathbf{p} = \sum_{n=0}^{\infty} c_n (2\kappa^{-2} \mathbf{K} - 1)^n \mathbf{p}. \quad (4.6.9)$$

The vector \mathbf{p} includes the acting force. In order to show this fact explicitly, we write

$$p_i = F_{i\sigma} k_\sigma \quad (4.6.10)$$

and identify F_{ji} to be

$$\begin{aligned} F_{ji} &= \frac{\partial p_j}{\partial k_i} = \sqrt{n_j \omega_j} e_j \delta_{ji} - e_j \sqrt{\frac{n_j}{\omega_j} \frac{n_i e_i^2}{n_\tau e_\tau^2 \rho_\tau}} \\ &= e_j \sqrt{n_j \omega_j} \left(\delta_{ji} - \frac{n_i e_i^2 \rho_j}{n_\tau e_\tau^2 \rho_\tau} \right). \end{aligned} \quad (4.6.11)$$

Substituting these into (4.6.9) and the result into (4.6.6), we finally obtain

$$\text{grad}_x \psi'_j(\mathbf{o}) = \frac{\kappa}{3 DkT} \frac{1}{\sqrt{n_j \omega_j}} \sum_{n=0}^{\infty} c_n (2\kappa^{-2} \mathbf{K} - 1)^n_{j\sigma} F_{\sigma\tau} k_\tau. \quad (4.6.12)$$

4.7. *Conversion to Practical Units.*

In order to compare with experimental results, we shall need formula (4.6.12) expressed in practical units. We recall the transformations made in the viscosity problem:

$$\Gamma_i = m_i z_i^2 = \frac{1000}{N\epsilon^2} n_i e_i^2 \quad (4.7.1)$$

$$\mu_i = \frac{\Gamma_i}{\Gamma} = \frac{n_i e_i^2}{n\sigma e\sigma^2} \quad (4.7.2)$$

$$\kappa^2 = \frac{N\epsilon^2}{1000} \frac{4\pi}{DkT} \Gamma \quad (4.7.3)$$

$$\omega_j = \frac{300}{\epsilon} \frac{\bar{u}_j^0}{z_j} = \frac{300}{96500} \frac{\Lambda_j^0}{\epsilon z_j} \quad (4.7.4)$$

$$M K M^{-1} = G', \quad m_{ji} = \delta_{ji} e_j \sqrt{n_j \omega_j} \quad (4.7.5)$$

$$h_{ij} = h'_{ji} = \frac{g'_{ji}}{\kappa^2} = \delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_j \frac{\omega_j}{\omega_j + \omega_i}. \quad (4.7.6)$$

In the migration problem, it will be more convenient to use the matrix H instead of its transposed H' ; we have

$$M^{-1} K M = G = \kappa^2 H$$

$$h_{ji} = \frac{g_{ji}}{\kappa^2} = \delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_i \frac{\omega_i}{\omega_j + \omega_i}. \quad (4.7.7)$$

The matrix H has pure numbers as its elements and so has $(1 - \kappa^{-1} G^{1/2}) = (1 - H^{1/2})$. The matrix H is not symmetrical; in this case, the eigenvectors \mathbf{x}_p and their adjoints \mathbf{x}_p^* are¹ defined by the following relations

$$\mathbf{H}' \mathbf{x}_p^* = \zeta_p \mathbf{x}_p^*; \mathbf{H} \mathbf{x}_p = \zeta_p \mathbf{x}_p; (\mathbf{x}_p, \mathbf{x}_q^*) = \delta_{pq} \quad (4.7.8)$$

where $\zeta_p = \alpha_p / \kappa^2$ are the characteristic numbers of H . The eigenvectors of H are readily connected with those of K by the following transformations:

$$\mathbf{K} \mathbf{l}_j = \alpha_j \mathbf{l}_j = \kappa^2 \mathbf{M} \mathbf{H} \mathbf{M}^{-1} \mathbf{l}_j,$$

whence

$$\mathbf{H} \mathbf{M}^{-1} \mathbf{l}_j = \zeta_j \mathbf{M}^{-1} \mathbf{l}_j \text{ and } \mathbf{x}_j = \mathbf{M}^{-1} \mathbf{l}_j. \quad (4.7.9a)$$

Likewise

$$\mathbf{K}' \mathbf{l}_j = \alpha_j \mathbf{l}_j = \kappa^2 \mathbf{M}^{-1} \mathbf{H}' \mathbf{M} \mathbf{l}_j,$$

whence

$$\mathbf{H}' \mathbf{M} \mathbf{l}_j = \zeta_j \mathbf{M} \mathbf{l}_j \text{ and } \mathbf{x}_j^* = \mathbf{M} \mathbf{l}_j. \quad (4.7.9b)$$

For the case of conduction without diffusion, the forces k_j equal $X e_j$, where X is the applied electric field. We substitute this in our general result (4.6.6) for $\text{grad}_x \psi'_j(\circ) = -\Delta X_j$ and obtain

¹ A trivial ambiguity remains in this definition, inasmuch as \mathbf{x}_p may be multiplied by a scalar λ_p while \mathbf{x}_p^* is divided by the same factor. In certain special cases, the ambiguity is greater, but still trivial as far as our purposes are concerned.

$$\begin{aligned}
-\frac{\Delta X_j}{X} &= \frac{\kappa}{3DkT} \frac{1}{\sqrt{n_j \omega_j}} \{M(1 - H^{1/2})M^{-1}\}_{j\sigma} F_{\sigma\tau} e_\tau \\
&= \frac{\kappa}{3DkT} e_j (1 - H^{1/2})_{j\sigma} \left(\delta_{\sigma\tau} - \frac{n_\tau e_\tau^2 \rho_\sigma}{n_\pi e_\pi^2 \rho_\pi} \right) e_\tau \\
&= \frac{\epsilon^3}{3} \sqrt{\frac{N\pi}{250k^3}} \frac{\Gamma^{1/2}}{(DT)^{3/2}} z'_j (1 - H^{1/2})_{j\sigma} r_\sigma
\end{aligned} \quad (4.7.10)$$

where \mathbf{r} is a vector defined by

$$r_i = \left(\delta_{i\tau} - \frac{n_\tau e_\tau^2 \rho_i}{n_\pi e_\pi^2 \rho_\pi} \right) z'_\tau = z'_i - \frac{z'_\tau \mu_\tau}{\mu_\pi z_\pi / \Lambda^\circ_\pi \Lambda^\circ_i} \quad (4.7.11)$$

The primes on the valences z'_i mean that they must carry the sign of the corresponding ionic charge. We note that the second term of r , vanishes for a symmetrical electrolyte ($z'_\tau \mu_\tau = 0$); in this case, the vector \mathbf{t} of (4.6.5) is already orthogonal to the eigenvector \mathbf{l}_1 . For convenience in numerical computation, we define vectors $\mathbf{r}^{(n)}$ by means of the recursion formula

$$r_j^{(n)} = (2H - 1)_{j\sigma} r^{(n-1)}_\sigma; r_j^{(0)} = r_j. \quad (4.7.12)$$

Then our formula becomes, on substituting numerical values for the universal constants ($N = 6.06 \times 10^{23}$; $k = 1.371 \times 10^{-16}$ erg/°; $\epsilon = 4.774 \times 10^{-10}$ e.s.u.) in (4.7.10),

$$\frac{\Delta X_j}{X} = 1.971 \times 10^6 \frac{\Gamma^{1/2}}{(DT)^{3/2}} z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} \quad (4.7.13)$$

where the coefficients c_n of the series expansion for $(1 - H^{1/2})$ are given by (4.6.8).

4.8. Conductance in Mixed Electrolytes.

We are now ready to compute the conductances in a mixture of s species of ions. The net field acting on an ion is $X + \Delta X_j$, where ΔX_j is the added field caused by the finite time of relaxation of the ionic atmosphere. Due to electrophoresis, the velocity v_j of the ion is less than $(X + \Delta X_j) e_j \omega_j$, which would correspond to the acting force $(X + \Delta X_j) e_j$, so that we have for the net velocity

$$v_j = X \left(e_j \omega_j + \frac{\Delta X_j}{X} e_j \omega_j - \frac{e_j \kappa}{6 \pi \eta} \right)$$

on substituting (4.2.11) for the electrophoretic correction. The mobility in electrostatic units is $u_j = |v_j|/X$, and in practical units for a potential gradient of one volt/cm is

$$\overline{u_j} = \frac{1}{300} \left(|e_j| \omega_j + \frac{\Delta X_j}{X} |e_j| \omega_j - \frac{|e_j| \kappa}{6 \pi \eta} \right).$$

The quantity $|e_j| \omega_j / 300$ is the limiting mobility $\overline{u_j^0}$ for infinite dilution. Since the equivalent conductance $\Lambda_j = 96500 \overline{u_j}$, we have

$$\Lambda_j = \Lambda^\circ_j + \frac{\Delta X_j}{X} \Lambda^\circ_j - \frac{\epsilon^2 965}{18} \sqrt{\frac{N}{250\pi k}} \frac{z_j \Gamma^{1/2}}{\eta (DT)^{1/2}}.$$

If we now substitute (4.7.13) and evaluate the constants, we obtain for our final result

$$\Lambda_j = \Lambda^\circ_j - \left(\frac{1.971 \times 10^6}{(DT)^{3/2}} \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + \frac{28.98 z_j}{\eta (DT)^{1/2}} \right) \Gamma^{1/2}. \quad (4.8.1)$$

For aqueous solutions at 25°, using Drake, Peirce and Dow's¹ value of the dielectric constant $D = 78.57$ and 0.00895 for the viscosity of water,

$$\Lambda_j = \Lambda^\circ_j - (0.5502 \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + 21.17 z_j) \Gamma^{1/2}, \quad (4.8.2)$$

and for 18°, using $D = 81.17$ and $\eta = 0.01056$,

$$\Lambda_j = \Lambda^\circ_j - (0.5429 \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + 17.85 z_j) \Gamma^{1/2}. \quad (4.8.3)$$

These formulas give the limiting law for the conductance of the j -th species of ions in a mixture of s different kinds. The electrophoretic correction of course depends only on the square root of the total ionic strength, but the relaxation correction depends also on the mobility ratios and on the ratios μ_1, \dots, μ_s in which the various ions are present. The nature of this dependence will be made clear by considering several numerical examples, although we can already see from (4.5.1) that the "mixture effect" will be greater, the more the mobility ratios deviate from unity.

4.9. Method of Computation.

For $s = 2$ or 3, the most convenient method of computation proceeds by (explicit or implicit) evaluation of the characteristic numbers of the matrix H . For $s = 2$, the characteristic numbers are $\zeta_1 = 1$ and $\zeta_2 = q$ (compare (3.8.29) in the viscosity discussion); then $(1 - \zeta_1) = 0$ and $(1 - H^{1/2})_{\sigma\sigma} r_\sigma$ reduces to $(1 - \sqrt{q}) r_j$. The result can be written in the form

$$\Lambda_j = \Lambda^\circ_j - \left(\frac{1.971 \times 10^6}{(DT)^{3/2}} \frac{q}{1 + \sqrt{q}} z_1 z_2 \Lambda^\circ_j - \frac{29.0 z_j}{\eta (DT)^{1/2}} \right) \Gamma^{1/2} \quad (4.9.1)$$

given previously by one of us.

For $s = 3$, H has three characteristic numbers, ζ_j , one of which is unity. In our formula, \mathbf{r} is orthogonal² to the eigenvector \mathbf{x}_1^* of H' because \mathbf{p} of (4.6.5) was constructed orthogonal to the eigenvector \mathbf{l}_1 of K . Then by using the properties of the eigenvectors,

$$\begin{aligned} (1 - H^{1/2}) \mathbf{r} &= (1 - H^{1/2}) \{ (\mathbf{x}_2^*, \mathbf{r}) \mathbf{x}_2 + (\mathbf{x}_3^*, \mathbf{r}) \mathbf{x}_3 \} \\ &= (1 - \zeta_2^{1/2}) (\mathbf{x}_2^*, \mathbf{r}) \mathbf{x}_2 + (1 - \zeta_3^{1/2}) (\mathbf{x}_3^*, \mathbf{r}) \mathbf{x}_3. \end{aligned} \quad (4.9.2)$$

¹ Drake, Peirce and Dow: Phys. Rev., **35**, 613 (1930).

² The proof is simple. By construction,

$$\mathbf{p} = (\mathbf{p}, \mathbf{l}_2) \mathbf{l}_2 + (\mathbf{p}, \mathbf{l}_3) \mathbf{l}_3$$

so that

$$\begin{aligned} \mathbf{M}^{-1} \mathbf{p} / X &= \mathbf{r} = (\mathbf{r}, \mathbf{M} \mathbf{l}_2) \mathbf{M}^{-1} \mathbf{l}_2 + (\mathbf{r}, \mathbf{M} \mathbf{l}_3) \mathbf{M}^{-1} \mathbf{l}_3 \\ &= (\mathbf{r}, \mathbf{x}_2^*) \mathbf{x}_2 + (\mathbf{r}, \mathbf{x}_3^*) \mathbf{x}_3 \end{aligned}$$

and since $(\mathbf{x}_1^*, \mathbf{x}_2) = (\mathbf{x}_1^*, \mathbf{x}_3) = 0$ by (4.7.8), \mathbf{r} has components only in the plane of \mathbf{x}_2 and \mathbf{x}_3 .

A straight line $y = a + bz$ will in general intersect the curve $y = 1 - z^{1/2}$ at 2 points; suppose we write $1 - z^{1/2} = a + bz$ and determine a and b so that the points of intersection will be ζ_2 and ζ_3 ; that is, we solve

$$1 - \sqrt{\zeta_2} = a + b \zeta_2$$

$$1 - \sqrt{\zeta_3} = a + b \zeta_3$$

for a and b and obtain

$$a = 1 - \frac{\sqrt{\zeta_2 \zeta_3}}{\sqrt{\zeta_2} + \sqrt{\zeta_3}}, \quad b = -\frac{1}{\sqrt{\zeta_2} + \sqrt{\zeta_3}}. \quad (4.9.3)$$

Then using again the properties of eigenvectors and the fact that \mathbf{r} is perpendicular to \mathbf{x}^* , we may write (as may be verified by substituting (4.9.3) and comparing with (4.9.2))

$$(1 - \mathbf{H}^{1/2}) \mathbf{r} = (a + b\mathbf{H}) \mathbf{r}, \quad (4.9.4)$$

and use this formula with the above values of a and b for numerical computation.

We obtain the characteristic values ζ_j by solving the cubic equation

$$|h_{ji} - \delta_{ji} \zeta| = (\zeta - \zeta_1)(\zeta - \zeta_2)(\zeta - \zeta_3) = 0.$$

Knowing $\zeta_1 = 1$, we only require the sum and the product of the two roots ζ_2 and ζ_3 . We write the cubic in the form

$$\zeta^3 - I_1 \zeta^2 + I_2 \zeta - I_3 = 0$$

and identify two invariants of the matrix \mathbf{H}

$$I_1 = \zeta_1 + \zeta_2 + \zeta_3 = h_{11} + h_{22} + h_{33} \quad (4.9.5)$$

and

$$\begin{aligned} I_2 &= \zeta_1 \zeta_2 + \zeta_2 \zeta_3 + \zeta_3 \zeta_1 = \\ &= h_{11} h_{22} + h_{22} h_{33} + h_{33} h_{11} - h_{12} h_{21} - h_{23} h_{32} - h_{31} h_{13}. \end{aligned} \quad (4.9.6)$$

Since $\zeta_1 = 1$,

$$\zeta_2 + \zeta_3 = I_1 - 1 \quad \text{and} \quad \zeta_2 \zeta_3 = I_2 - I_1 + 1.$$

We have to calculate

$$\sqrt{\zeta_2 \zeta_3} = (I_2 - I_1 + 1)^{1/2}, \quad \zeta_2 + \zeta_3 = I_1 - 1,$$

and

$$\sqrt{\zeta_2} + \sqrt{\zeta_3} = \sqrt{(\zeta_2 + \zeta_3) + 2\sqrt{\zeta_2 \zeta_3}}$$

from the elements of the matrix \mathbf{H} by using (4.9.5) and (4.9.6). This gives the following values for the constants of (4.9.4)

$$a = 1 - \frac{\sqrt{I_2 - I_1 + 1}}{\sqrt{I_1 - 1 + 2\sqrt{I_2 - I_1 + 1}}} \quad (4.9.7)$$

$$b = \frac{-1}{\sqrt{I_1 - 1 + 2\sqrt{I_2 - I_1 + 1}}}. \quad (4.9.8)$$

For three ions of valence ± 1 , one of the ionic ratios, say μ_3 is $1/2$, so that $\mu_2 = \frac{1}{2} - \mu_1$, and we may express all the elements of H in terms of μ_1 . If we define

$$\omega_{ji} = \frac{\omega_j}{\omega_i + \omega_j} \quad \text{where } \omega_{ij} + \omega_{ji} = 1, \omega_{jj} = 1/2,$$

then

$$h_{ji} = \mu_\sigma \omega_{\sigma j} \delta_{ji} + \mu_i \omega_{ij}. \quad (4.9.9)$$

4.10. Examples of Computation.

We shall now illustrate this method by computing the conductance at 18° for a solution containing 0.02 mols HCl and 0.08 mols KCl per liter. Then, using Kohlrausch's values of Λ° , we have the following data:

<i>Ion</i>	<i>j</i>	$m_j = \Gamma_j$	μ_j	Λ_j°	
H ⁺	1	0.02	0.1	315	$\omega_{12} = 0.8298$
K ⁺	2	0.08	0.4	64.6	$\omega_{13} = 0.8279$
Cl ⁻	3	0.10	0.5	65.5	$\omega_{23} = 0.4965$

The matrix H is

$$\begin{pmatrix} 0.2541 & 0.0681 & 0.0860 \\ 0.0830 & 0.7348 & 0.2518 \\ 0.0828 & 0.1986 & 0.7814 \end{pmatrix}.$$

and the invariants are

$$I_1 = 1.6712 + 0.9910 \mu_1 = 1.7703$$

$$I_2 = 0.7567 + 1.3772 \mu_1 + 0.2186 \mu_1^2 = 0.8966.$$

Then, using (4.9.4), (4.9.7) and (4.9.8)

$$(1 - H^{1/2}) = 0.7080 - 0.8217 H.$$

Since we are dealing with symmetrical electrolytes, the second term of the vector \mathbf{r} in (4.7.11) vanishes, and \mathbf{r} has the components $r_1 = 1, r_2 = 1, r_3 = -1$. The product (4.9.4) is now readily evaluated:

$$\begin{aligned} (1 - H^{1/2})_{1\sigma} r_\sigma &= 0.7080 r_1 - 0.8217 H_{1\sigma} r_\sigma \\ &= 0.7080 - 0.8217 (0.2541 + 0.0681 - 0.0860) = 0.5139 \\ (1 - H^{1/2})_{2\sigma} r_\sigma &= 0.2429 \text{ and } (1 - H^{1/2})_{3\sigma} r_\sigma = -0.2971. \end{aligned}$$

By (4.7.13) and (4.6.7), with $\Gamma = 0.2$,

$$-\frac{\Delta X_j}{X} = 0.5416 \Gamma^{1/2} z'_j (1 - H^{1/2})_{j\sigma} r_\sigma = 0.2423 z'_j (1 - H^{1/2})_{j\sigma} r_\sigma. \quad (4.10.1)$$

Now $\Delta X_j/X$ measures the relaxation correction to the conductance. Since the electrophoretic correction is independent of μ_1 , we shall find it most interesting to confine our attention to the first correction. For either pure HCl or KCl at a concentration $\Gamma = 0.2$,

$$-\Delta X_j/X = 0.159 \Gamma^{1/2} = 0.0711$$

for each ion.¹

¹ Onsager: II, equation (65).

We have tabulated in the first column below $\Delta X_j/X$ calculated by means of (4.10.1) for the mixture of HCl and KCl under consideration; the second column $\Delta\Lambda_j/\Lambda^\circ$ gives the difference between these figures and 0.0711, reckoned as percent change of conductance, and the third column the corresponding changes $\Delta\Lambda_j$ in conductance.

TABLE I

j	$\Delta X_j/X$	100 $\Delta\Lambda_j/\Lambda^\circ$	$\Delta\Lambda_j$
1	0.1245	-5.34	-16.8
2	0.0589	+1.22	+ 0.79
3	0.0720	-0.09	- 0.07

Assuming that our limiting laws (4.8.1) were valid at a concentration $\Gamma = 0.2$, the conductance of hydrogen ion in the 4 to 1 mixture would be 16.8 units less than in 0.1 normal HCl ($\Gamma = 0.2$), that of the potassium ion would be increased by 0.8 units over its value in 0.1 normal KCl and that of the chloride ion decreased by about 0.1 unit. Actually, this concentration is in general too high for applying the limiting formulas of the electrostatic theory, but we may assume that the *difference* in conductance in a mixture and in a solution containing a single solute at the same ionic strength would be given by (4.8.1) to the right order of magnitude at least, and that the calculated difference for a given ion would agree more closely with experiment, the lower the total concentration of ions. We shall see in the following section that these predictions are verified.

For $s = 4$, the equation $|h_{ji} - \delta_{ji} \zeta| = 0$ which determines the characteristic numbers is of the fourth degree, and although one of these numbers ($\zeta_1 = 1$) is known, it is not convenient in general to compute the others. Expansion of the function $(1 - H^{1/2})$ in a series will prove to be the most satisfactory method. We shall illustrate this method by computing the conductance changes at 18° in a solution containing 0.04995 mols HCl and 0.0502 mols KCl per liter; the method for $s = 4$ is entirely analogous. Our data are then as follows:

Ion	j	$m_j = \Gamma_j$	μ_j	Λ°_j
H ⁺	1	0.04995	0.2495	315
K ⁺	2	0.05016	0.2505	64.6
Cl ⁻	3	0.1001	0.5000	65.5

The matrices are

$$(h_{ji}) = \begin{pmatrix} 0.3782 & 0.0426 & 0.0860 \\ 0.2070 & 0.7094 & 0.2518 \\ 0.2066 & 0.1244 & 0.8310 \end{pmatrix}$$

$$(2h_{ji} - \delta_{ji}) = \begin{pmatrix} -0.2436 & 0.0853 & 0.1721 \\ 0.4140 & 0.4188 & 0.5036 \\ 0.4132 & 0.2488 & 0.6620 \end{pmatrix}$$

By means of the recursion formula (4.7.12) we now compute the vectors $\mathbf{r}^{(n)}$, for example

$$r^{(1)}_1 = (2H - 1)_{1\sigma} r_\sigma = (-0.2436 + 0.0853 - 0.1721) = -0.3304.$$

The following table gives the first four:

TABLE II

n	$r^{(n)}_1$ +1	$r^{(n)}_2$ +1	$r^{(n)}_3$ -1
1	-0.3304	0.3292	0.0000
2	0.1086	0.0011	-0.0546
3	-0.0358	0.0180	0.0091
4	0.0118	-0.0027	-0.0043

The sums $\sum_{n=0}^{\infty} c_n r^{(n)}_j$ may now be evaluated, using the values of the coefficients c_n given in (4.6.8); the first five terms of the series already give four place accuracy. The results of the calculations are given below, where the symbols are the same as those used in Table I.

TABLE III

Ion	j	$z'_j \Sigma c_n r^{(n)}_j$	$\Delta X_j / X$	$100 \Delta \Lambda_j / \Lambda^\circ_j$	$\Delta \Lambda_j$
H ⁺	1	0.4212	0.1020	-3.09	-9.72
K ⁺	2	0.1758	0.0426	+2.85	+1.84
Cl ⁻	3	0.2982	0.0723	-0.12	-0.08

The change of hydrogen ion conductance $\Delta \Lambda_1$ for an infinitesimal amount of HCl in 0.1 normal KCl is readily obtained by setting μ_1 zero: the following figures are self-explanatory:

$$(h_{j1}) = \begin{pmatrix} 0.1712 & 0.0851 & 0.0861 \\ 0 & 0.7518 & 0.2518 \\ 0 & 0.2483 & 0.7483 \end{pmatrix}$$

$$I_1 = 1.6712; \quad I_2 = 0.7567$$

$$(1 - H^{1/2}) = 0.7391 - 0.8922 H = a + bH$$

TABLE IV

j	r_j	$H_{j\sigma} r_\sigma$	$z'_j (a + bH)_{j\sigma} r_\sigma$	$\Delta X_j / X$	$100 \Delta \Lambda_j / \Lambda^\circ_j$	$\Delta \Lambda_j$
1	1	0.1702	0.5872	0.1423	7.13	22.4
2	1	0.5000	0.2930	0.0710	0	0
3	-1	0.5000	0.2930	0.0710	0	0

Our result is that the limiting equivalent conductance of hydrogen ion in 0.1 KCl would be 22.4 units less than the conductance of hydrogen ion in 0.1 HCl. This is the result calculated by Bennewitz, Wagner and K  chler who have given a solution of the general equation (4.4.2) for the case $s = 3$, valid when one of the ions is present in infinitesimal amount.

4.11. Comparison with Experiment.

The change of conductance due to the "mixture effect" has been computed for several sets of published data. Bennewitz, Wagner and K  chler¹ have de-

¹ Bennewitz, Wagner and K  chler: Loc. cit.

terminated the transference numbers of Ba^{++} , H^+ , K^+ and Cl' in various mixtures of BaCl_2 and HCl and of KCl and HCl at 18° . The concentrations used in our two examples in the description of the method of computation were taken from their data. Table V compares their observed results with our computed values:

TABLE V

	0.05 KCl - 0.05 HCl		0.08 KCl - 0.02 HCl	
	<i>calc.</i>	<i>obs.</i>	<i>calc.</i>	<i>obs.</i>
$\Delta\Lambda_1(\text{H}^+)$	-9.72	-10	-16.8	-12.8
$\Delta\Lambda_2(\text{K}^+)$	+1.84	+0.9	+0.8	—

Longworth¹ has measured the migration velocities of individual ions in mixtures of HCl and KCl at 25° in which the chloride ion concentration was kept constant at 0.1 normal ($\Gamma = 0.2$). Table VI compares his results with those calculated² by means of (4.8.2).

TABLE VI

μ_1	$\Delta\Lambda_1(\text{H}^+)$		$\Delta\Lambda_2(\text{K}^+)$		$\Delta\Lambda_3(\text{Cl}')$	Λ_3
	<i>calc.</i>	<i>obs.</i>	<i>calc.</i>	<i>obs.</i>	<i>calc.</i>	<i>obs.</i>
0.500 ^a	0.00	—	+3.86	(2.36)	0.000	66.32
0.375	-5.14	-2.56	3.00	2.06	0.063	66.19
0.250	-10.81	-5.06	2.09	0.96	0.097	66.07
0.125	-17.24	-8.06	1.10	0.56	0.086	65.83
0.000 ^b	-24.79	(-10.96)	0.00	—	0.000	65.75

^a pure HCl

^b pure KCl .

The "observed" values in parentheses were obtained by Longworth by linear extrapolation of his data. Fig. 4 summarizes the calculated and observed results for H^+ and Fig. 5 for K^+ . Bennewitz' data are indicated by crosses, Longworth's by circles and the theoretical curve is drawn solid. The theoretical curve depends on the mixing ratio in a rather complicated way; both graphs exhibit a slight curvature. Longworth's results lie on a smooth curve which is approximately of the same form as the theoretical, although due to the high concentration, the numerical values differ by about a factor of two. Bennewitz, Wagner and K  chler obtained their results by the Hittorf method, while Longworth employed the method of moving boundaries. The latter method is probably capable of greater accuracy, and in fact, the effects measured by Longworth fall beneath the calculated values by amounts that might reasonably correspond to the mathematical approximations allowed in the theory.

¹ Longworth: J. Am. Chem. Soc., **52**, 1897-1910 (1930).

² We used the following values in order to compute the results for the 25° experiments:

$\Lambda_\infty(\text{HCl}) = 426.0$, $\Lambda_\infty(\text{NaCl}) = 126.42$, $\Lambda_\infty(\text{KCl}) = 149.84$; $t_K(\text{KCl}) = 0.4905$.

t_K = limiting transference number of K^+ in KCl . We are indebted to Dr. MacInnes, Dr. Longworth and Dr. Shedlovsky for permission to use these figures in advance of their publication.

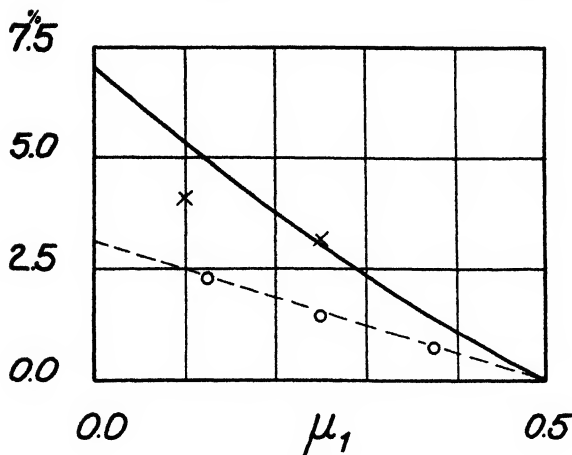


FIG. 4

Variation of Hydrogen Ion Conductance in HCl-KCl Mixtures

Fig. 6 shows the calculated mixture effect for the common ion (Cl' in HCl and KCl); the effect is so small that it was necessary to magnify the scale (50 times compared to figures 4 and 5). The maximum effect is apparently within the experimental error, and as seen from Table VI, is masked by a specific difference in Λ_{Cl} between HCl and KCl; we have therefore tabulated Λ_3 instead of $\Delta\Lambda_3$.

As a final example, we have chosen the data of Bray and Hunt¹ on the specific conductance of mixtures of NaCl and HCl at 25°. If there were no mixture effect, one could compute the specific conductance κ of a solution containing m_1 mols NaCl and m_2 mols HCl from the conductance Λ_{NaCl} of NaCl in m_1 normal solution and that of HCl, Λ_{HCl} , in m_2 HCl by the formula

$$1000\kappa = m_1\Lambda_{\text{NaCl}} + m_2\Lambda_{\text{HCl}}.$$

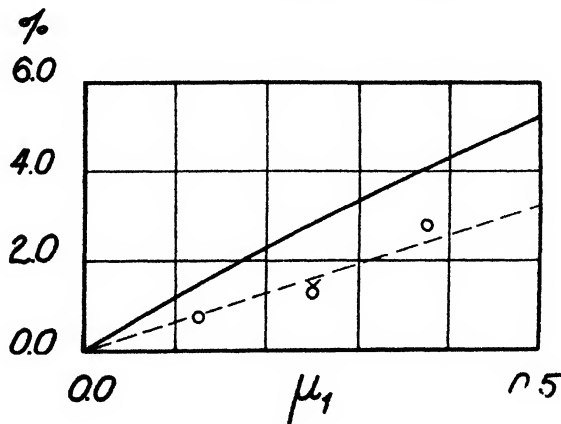


FIG. 5

Variation of Potassium Ion Conductance in HCl-KCl Mixtures

¹ Bray and Hunt: J. Am. Chem. Soc., 33, 781 (1911).

These values have been computed from Bray and Hunt's data on pure NaCl and pure HCl solutions. Then the observed specific conductances were subtracted from the additive conductances, to give " $\Delta\kappa$ observed", the deviations from additivity due to the mixture effect. By means of (4.8.2), we calculated the change of conductance due to the presence of 3 kinds of ions as before, and then computed the sum $m_1\Delta\Lambda_1 + m_2\Delta\Lambda_2 + m_3\Delta\Lambda_3$ as " $\Delta\kappa$ calculated." The results are given in Table VII: (concentrations in millimols).

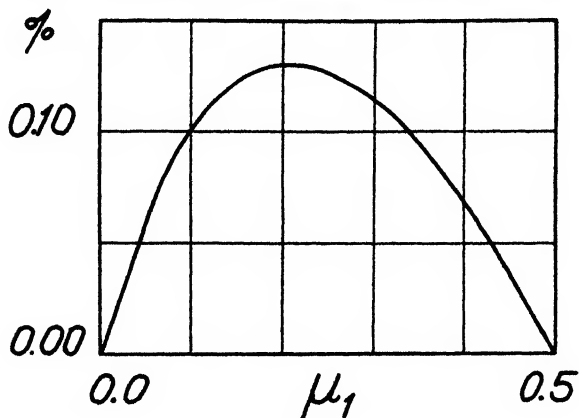


FIG. 6

Variation of Chloride Ion Conductance in HCl-KCl Mixtures

TABLE VII

Conc. HCl	Conc. NaCl	$\Delta\kappa \times 10^3$ obs.	$\Delta\kappa \times 10^3$ calc.	% obs.	% calc.
100	100	0.94	1.56	1.99	3.31
50*	100	0.50	0.95	1.72	3.29
20*	100	0.26	0.45	1.44	2.50
10	100	0.15	0.24	1.05	1.68
5	100	0.08	0.12	0.64	0.98
2	100	0.04	0.05	0.35	0.42
50	20	0.17	0.248	0.78	1.14
20	20	0.103	0.139	1.02	1.38
10	20	0.061	0.085	0.98	1.35
4	20	0.034	0.040	0.88	1.03
2	20	0.021	0.021	0.68	0.71
1	20	0.011	0.011	0.40	0.41
12.5	5	0.028	0.0311	0.50	0.55
5	5	0.020	0.0174	0.76	0.66
2.5	5	0.010	0.0106	0.62	0.65
1	5	0.005	0.0050	0.49	0.49

The two experiments marked with an asterisk are in about the same range of concentration and mixing ratio as the KCl-HCl mixtures discussed above, and again the calculated result is about twice the observed. It will be noted, however, that the calculated figures agree more closely with experiment, the smaller μ_1 and Γ become. Also, the calculated values for $\Delta\kappa$ duplicate the observed flat maximum of $\Delta\kappa$ at the equal mixture of NaCl and HCl.

The experiments of Bray and Hunt indicate that if the individual mobilities in a mixture were measured at low concentrations, not only the type, but also the absolute magnitude of the mixture effect would be found to agree with the theory.

4.12. *The General Equations for Diffusion.*

Fick's law for diffusion in a two-component system is ordinarily written

$$c \mathbf{v} = \mathbf{J} = -D \text{ grad } c, \quad (4.12.1)$$

where D is the coefficient of diffusion, \mathbf{v} the velocity, \mathbf{J} the flow and c the concentration (amount per unit volume) of solute. The flow is usually defined relative to a fixed plane in the solution, which is assumed "at rest." This convention has the esthetic advantage that no distinction is made between solute and solvent, both obeying (4.12.1) with the same coefficient of diffusion D . Moreover, the ideal case of "self-diffusion" (interdiffusion of isotopes) is most simply described in this form; D becomes independent of the mixing ratio. In a general case, however, it is somewhat awkward to define a solution "at rest" during diffusion, particularly when the mixing of the substances involved causes an appreciable change of volume. We must bear in mind that the concentration gradient determines only the local *relative* flow of solute and solvent, and that a bulk motion of the solution, dependent on other conditions, may be superimposed.

In the following, we shall assume that one (solvent) constituent of the solution is present in dominating quantity. The flow of any solute constituent will be defined *relative to a local frame of reference moving with the solvent*. This simpler convention seems definitely preferable in the case of electrolytes, which are in any case hardly amenable to a symmetrical consideration of solute and solvent. If a symmetrical formulation is desired, one may define a "bulk velocity"

$$\bar{\mathbf{v}} = \sum \mathbf{J}_i \bar{V}_i = \sum c_i \mathbf{v}_i \bar{V}_i, \quad (4.12.2)$$

where $(\bar{V}_0), \bar{V}_1, \dots, \bar{V}_s$ are the partial volumes of the constituents (o), 1, \dots , s ; apparently there is no reasonable alternative to this choice. We may assume that either the velocity of the solvent or the "bulk velocity" (4.12.2) obeys the hydrodynamic laws; the difference is of no practical importance.

Fick's law (4.12.1) may be written in the alternative form

$$\mathbf{J} = -\Omega \text{ grad } \mu, \quad (4.12.3)$$

where μ is the chemical potential, and the coefficient of diffusion equals

$$D = \Omega(\partial\mu/\partial c)_{P,T}. \quad (4.12.4)$$

In the special case of an ideal solution

$$\partial\mu/\partial c = RT/c,$$

so that

$$RT \Omega = cD.$$

In general, (4.12.4) may be rewritten in terms of activity coefficients f :

$$cD = RT\Omega (1 + c \partial \log f / \partial c). \quad (4.12.5)$$

In the case of electrolytes, the correction term involving f is negative, except in some cases at relatively high concentrations (cf. § 4.13). It has been suggested that the variation of D with concentration might be accounted for entirely by this deviation from ideal thermodynamic behavior, and that $\Omega/c = \text{const.}$ As we shall see in the following, the theory predicts that Ω/c will also vary with the concentration, although much less than D . According to (4.12.3), the ratio Ω/c equals the "mobility," that is the velocity caused by a unit force $\mathbf{k} = -\text{grad } \mu$, (cf. § 4.1).

The natural generalization of (4.12.3) to the case of several solute substances is

$$\mathbf{J}_i = -\sum_{k=1}^s \Omega_{ik} \text{grad } \mu_k, \quad (i = 1, \dots, s), \quad (4.12.6)$$

assuming a linear relation between velocities and potential gradients for the solute substances 1, 2, . . . , s . The matrix of coefficients (Ω_{ik}) is symmetrical

$$\Omega_{ik} = \Omega_{ki}. \quad (4.12.7)$$

This reciprocal relation states that the flow of constituent no. 7 caused by a unit force per unit amount of no. 3 will equal the flow of no. 3 caused by a unit force on substance no. 7. Relations of this type are included in the "principle of the least dissipation of energy," which has been derived¹ from the assumption of microscopic reversibility. We shall show at the end of this section, assuming the principle of the least dissipation, that the symmetry relation (4.12.7) applies independently of the frame of reference for the flow, which is not quite obvious.

By solving the system of equations (4.12.6) for $\text{grad } \mu_1, \dots, \text{grad } \mu_s$, we obtain an alternative formulation of some interest, namely

$$-\text{grad } \mu_i = \sum_{k=1}^s R_{ik} \mathbf{J}_k, \quad (i = 1, \dots, s), \quad (4.12.8)$$

where the coefficients (R_{ik}) form the reciprocal matrix of (Ω_{ik}), and on account of the symmetry of the latter,

$$R_{ik} = R_{ki}. \quad (4.12.9)$$

Thanks to this symmetry, we only need to know the *dissipation-function*

$$2 F(\mathbf{J}, \mathbf{J}) = \sum_{i,k=1}^s R_{ik} (\mathbf{J}_i, \mathbf{J}_k) = \sum_{i,k} n_i n_k R_{ik} ((\mathbf{v}_i - \mathbf{v}_0), (\mathbf{v}_k - \mathbf{v}_0)), \quad (4.12.10)$$

and (4.12.8) may be written

$$\text{grad } \mu_i + \partial F / \partial \mathbf{J}_i = 0, \quad (i = 1, \dots, s), \quad (4.12.11)$$

¹ L. Onsager: Phys. Rev., 37, 405 (1931).

or in a variation-principle for convenient transformation

$$\delta(T\dot{S} - F) = 0, \quad (4.12.12)$$

where \dot{S} is the rate of production of entropy; according to thermodynamics

$$T dS/dt = T\dot{S} \equiv -\sum (\mathbf{J}_i \cdot \text{grad } \mu_i). \quad (4.12.13)$$

The formulation (4.12.12) satisfies all esthetic requirements.

In the case of an ideal solution containing solute molecules of the species $1, \dots, s$, the solute molecules might be expected to diffuse *independently* according to the law

$$\mathbf{J}_i = -\Omega_{ii} \text{grad } \mu_i, \quad (i = 1, \dots, s); \quad (4.12.14)$$

it also seems probable that the mobilities Ω_{ii}/c_i would not vary more with the composition than the fluidity of the solution. In the case of a solution that exhibits deviations from the ideal laws due to compound formation between the solute substances, we should expect that one migrating substance could carry another along, and that the coefficients Ω_{ik} , ($i \neq k$), would not all vanish. On this picture, if the simple law (4.12.14) is valid for the different species of molecules and molecular compounds actually present, the reciprocal relation (4.12.14) evidently holds. In many instances, however, attempts to describe all deviations from ideal laws in terms of molecular compounds lead to awkward difficulties, and the interpretation is usually ambiguous. Therefore, where a noncommittal phenomenological description will not suffice, it is preferable, when possible, to construct a more detailed physical picture, and to allow explicitly for the forces between the molecules. This applies particularly to electrolytes.

In dealing with electrolytes, it is convenient to describe conduction and diffusion by one combined scheme, so that (4.12.6) now relates the rates of flow $\mathbf{J}_1, \dots, \mathbf{J}_s$ of *ionic* species $1, \dots, s$ to the gradients of the *total potentials*

$$\mu_i = \mu_i' + e_i \varphi, \quad (4.12.15)$$

of the ions, where φ is the electrostatic potential, (cf. § 4.1). The generalization to the case where the electric field does not possess a potential is obvious. In the limit of low concentrations, the ions migrate independently (ideal case)

$$\begin{aligned} \Omega_{ik} &= 0, \quad (i \neq k); \\ \Omega_{ii} &= n_i \omega_i, \end{aligned}$$

where ω_i is the "mobility" of a single ion (in this notation, the electrolytic electrolytic mobility is $e_i \omega_i$ where e_i is the charge). At higher concentrations as shown by our calculations in §§ 4.1-7, the ions will interfere with each others' motion; the order of magnitude of this effect is given by

$$\Omega_{ik} = O(n_i n_k 4\pi \omega_i d_o^2 / \kappa) \pm O(n_i n_k d_o / \kappa \eta),$$

with $d_o = |e_i e_k| / DkT$ and otherwise the notations of §§ (1.3) and (4.1); the first term is due to direct transfer of forces, the second to electrophoresis. There are similar corrections to Ω_{ii} :

$$\Omega_{ii} = n_i \omega_i - O(n_i \omega_i \kappa d_o) - O(n_i^2 d_o / \kappa \eta).$$

Since $\kappa \sim n^{1/2}$, the relative effects of interaction are proportional to the square root of the concentration, in the sense that doubling all concentrations increases the effects by a factor $\sqrt{2}$.

The symmetry condition (4.12.7) for (Ω_k) holds for the migration of ions as well, if we allow the assumption of microscopic reversibility. While this assumption is nowhere explicitly introduced into our calculations, we shall see that the results conform to the reciprocal relation (4.12.7). The reason is, of course, that the assumed mechanism of interaction between the ions is in accord with the general principle. Indeed: The forces between the ions possess a potential, and so does the Brownian motion, because the relation of neighborhood is a reciprocal one; the hydrodynamic interaction of ions also obeys the same reciprocal relations because the principle of the least dissipation of energy¹ is valid for (slow) motion of viscous fluids.

The equations for migration of ions may be given the form (4.12.8) or (4.12.11-12); in the case of ions, μ_1, \dots, μ_s in (4.12.13) stand for the total potentials (4.12.15). The results of our calculations will be summarized in a very compact form by the construction of a dissipation-function.

We have promised to derive the reciprocal relation (4.12.7) from the principle of the least dissipation. We shall prefer to obtain its equivalent (4.12.9). Let us consider a case of parallel flow in unit cross-section, so that the volume element $dV = dx$. The flow J_i is defined relative to a frame of reference (ξ, y, z) which may move with the velocity of the solvent, or with the "bulk velocity" (4.12.2); in the latter case we could assume $\xi = x$. In any case there exists a *dissipation-function*

$${}_2 F \equiv {}_2 T\Phi \equiv \int \sum R_{ik} J_i J_k dx.$$

In order to apply the general principle (4.12.12)

$$\delta(\dot{S} - \Phi) = 0,$$

we must express \dot{S} in the variables J_i . For this purpose, write

$$n_k dx/d\xi = N_k,$$

then $N_k d\xi$ is the amount of k ions contained in the deformable volume element $d\xi$. According to thermodynamics

$$T(\dot{S} + \dot{S}^*) = - \int_{x'}^{x''} \sum \mu_k \frac{dN_k}{dt} d\xi - \sum [\mu_k J_k]_{x'}^{x''},$$

where \dot{S}^* , corresponding to the term in brackets, denotes the external entropy change (omitted above for simplicity). Now the equation of continuity

$$\frac{\partial J_k}{\partial \xi} = - \frac{\partial N_k}{\partial t}$$

is valid in deformable coordinates as well, hence

¹ This principle may be stated: When a force of magnitude X , applied at a point A in the direction (1), will cause a velocity v in the direction (2) at the point B , then conversely, the force X applied at B in the direction (2) will cause a velocity v in the direction (1) at A .

$$T\dot{S} = \int_{x'}^{x''} \sum \mu_k \frac{dJ_k}{d\xi} d\xi = \int_{x'}^{x''} \sum \mu_k dJ_k = \\ = \sum [\mu_k J_k]_{x'}^{x''} - \int_{x'}^{x''} \sum J_k d\mu_k$$

and

$$T(\dot{S} + \dot{S}^*) = - \int_{x'}^{x''} \sum J_k d\mu_k = - \int_{x'}^{x''} \sum J_k d\mu_k dx.$$

Now the principle of the least dissipation yields

$$0 = T \delta(\dot{S} + \dot{S}^* - \Phi) = \\ = \int_{x'}^{x''} \sum_i \left(- \frac{\partial \mu_i}{\partial x} - \frac{1}{2} \frac{\partial}{\partial J_i} (\sum_{k,j} R_{kj} J_k J_j) \right) \delta J_i dx = 0,$$

whence

$$- \frac{\partial \mu_i}{\partial x} = \sum_k R_{ik} J_k,$$

where

$$R_{ik} = R_{ki},$$

because the linear form is obtained by differentiation of a quadratic.

4.12. Diffusion of a Simple Electrolyte.

In an electrolyte containing only two kinds of ions, the condition for no electric current is that anions and cations migrate with the same velocity

$$v_1 = v_2 = v; \quad J_1 = n_1 v; \quad J_2 = n_2 v. \quad (4.13.1)$$

In the limit of low concentrations, the interaction between ions (except the space charge that prevents an electric current) may be neglected, and we have

$$v = k_1 \omega_1 = k_2 \omega_2 = -\omega_1 \text{ grad } \mu_1 = -\omega_2 \text{ grad } \mu_2. \quad (4.13.2)$$

In this "zero" approximation, the "forces" k_1 and k_2 on the individual ions are given by (4.13.2) and

$$k = \nu_1 k_1 + \nu_2 k_2 = -\text{grad } \mu,$$

where μ is the chemical potential of a molecule dissociating into ν_1 anions and ν_2 cations. We obtain

$$k_1 = \frac{-\rho_1}{\nu_1 \rho_1 + \nu_2 \rho_2} \text{ grad } \mu = \frac{-\omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \text{ grad } \mu;$$

$$k_2 = (\rho_2/\rho_1) k_1 = (\omega_1/\omega_2) k_1, \quad (4.13.3)$$

and

$$v = \frac{-\omega_1 \omega_2}{\nu_1 \omega_1 + \nu_2 \omega_2} \text{ grad } \mu. \quad (4.13.4)$$

Here, if the solution is assumed ideal in regard to its thermodynamic properties, so that

$$\text{grad } \mu = (\nu_1 + \nu_2) (kT/n) \text{ grad } n,$$

Nernst's formula¹

$$J = n v = - \frac{(\nu_1 + \nu_2)}{\nu_1 \omega_1 + \nu_2 \omega_2} \omega_1 \omega_2 kT \text{ grad } n \quad (4.13.5)$$

¹ Nernst: Loc. cit.

results. When the forces between the ions are taken into account, the main effect consists in a contribution to the thermodynamic potential; we have now

$$\text{grad } \mu = (\nu_1 + \nu_2) kT \text{ grad } \log (fn), \quad (4.13.6)$$

where f is the mean activity coefficient of the ions, for low concentrations¹ given by the limiting law

$$\log f = e_1 e_2 \kappa / 2 D k T. \quad (4.13.7)$$

We thus allow for the interionic attraction reducing the "thermodynamic" tendency of the ions to separate by diffusion; it remains to compute the effect of interaction on the *mobility* of the migrating ions.

We first note that the diffusion of a *simple* electrolyte will not be obstructed by the effect which Debye and Hückel named "ionic forces," the retardation of a migrating ion by an asymmetric field in its atmosphere. The reason is that all ions migrate with the same velocity, so that an atmosphere needs no coercion to follow its central ion; in consequence, the atmosphere is displaced as a whole, undisturbed, and develops no asymmetry. This can be verified already in our fundamental equations (4.3.2) by substituting

$$\mathbf{k}_1 \omega_1 = \mathbf{k}_2 \omega_2;$$

the perturbation terms in (4.3.2) then cancel each other. (In calculating the first approximation for the effect, we may compute the perturbation terms from the "zero" approximation (4.13.2).). Of course, our final formulas for the "ionic forces" also yield a vanishing effect for this case; we may refer to formula (4.14.12) below.

Otherwise with the electrophoresis, this effect depends on a *volume force* attacking in the ionic atmosphere. According to (4.2.2) and (4.2.6), if the potential at a distance r from a j ion is $\psi_j(r)$, then the force density at this distance is

$$\mathbf{F} = -(n_1 e_1 \mathbf{k}_1 + n_2 e_2 \mathbf{k}_2) (\psi_j / kT) + \frac{1}{2} (n_1 e_1^2 \mathbf{k}_1 + n_2 e_2^2 \mathbf{k}_2) (\psi_j / kT)^2 - \dots \quad (4.13.8)$$

Substituting (4.13.2), the first term in (4.13.8) vanishes when and only when $\omega_1 = \omega_2$; the second term is always positive. In § 4.2, we calculated the effect of the volume force (4.13.8) on the motion of the ions (assuming $\mathbf{k}_j = \nabla \rho_j$) and found for the resulting additional velocity (4.2.12)

$$\begin{aligned} \Delta \mathbf{v}_j = \nabla \left(-\frac{2}{3\eta} (n_1 e_1 \rho_1 + n_2 e_2 \rho_2) \frac{e_j}{DkT \kappa(1 + \kappa a)} \right. \\ \left. + \frac{1}{3\eta} (n_1 e_1^2 \rho_1 + n_2 e_2^2 \rho_2) \left(\frac{e_j}{DkT} \right)^2 \varphi(\kappa a) \right), \quad (4.13.9) \\ (j = 1, 2) \end{aligned}$$

with

$$\varphi(\kappa a) = e^{2\kappa a} \text{Ei}(2\kappa a) / (1 + \kappa a)^2. \quad (4.13.10)$$

The ultimate result of this effect is of course to alter the forces \mathbf{k}_1 and \mathbf{k}_2 that are needed to make both ions migrate with the same velocity \mathbf{v} : because in

¹ Debye and Hückel: Physik. Z., 24, 185 (1923).

pure diffusion, any velocity difference $\mathbf{v}_1 - \mathbf{v}_2$ will be eliminated by a readjustment of the electric field (space charge). Since both ions migrate relative to a moving immediate environment, we have now

$$\mathbf{k}_j = \rho_j(\mathbf{v} - \Delta\mathbf{v}_j), \quad (j = 1, 2). \quad (4.13.11)$$

Strictly speaking, this corrected force should be substituted in (4.13.9) in order to calculate $\Delta\mathbf{v}_j$, but our calculations are not accurate enough to warrant this refinement. When we use (4.13.9), as stands, for calculating the correction to \mathbf{k} , we obtain (cf. (4.2.13-14))

$$\begin{aligned} -\text{grad } \mu = \mathbf{k} &= \nu_1\rho_1(\mathbf{v} - \Delta\mathbf{v}_1) + \nu_2\rho_2(\mathbf{v} - \Delta\mathbf{v}_2) = \\ &= \mathbf{v} \left(\nu_1\rho_1 + \nu_2\rho_2 + (\rho_1 - \rho_2)^2 \frac{\nu_1\nu_2}{(\nu_1 + \nu_2)} \frac{\kappa}{6\pi\eta(1 + \kappa a)} \right. \\ &\quad \left. - \left\{ \frac{\nu_2\rho_1 + \nu_1\rho_2}{\nu_1 + \nu_2} \right\}^2 \frac{\kappa^4\varphi(\kappa a)}{48\pi^2\eta n} \right) \end{aligned} \quad (4.13.12)$$

for the "force" per molecule of solute (present in concentration $n = n_1/\nu_1 = n_2/\nu_2$ molecules/cm³). The third term in the brackets is the "first order" electrophoretic effect, proportional to \sqrt{n} (for $\kappa a \ll 1$). The last term is of the order $n \log n$, (second order), and always negative. The physical interpretation of the effect is interesting. If the ions were arranged at random, then the assembly of ions, moving as a whole with the velocity \mathbf{v} against the solvent, would meet the same resistance as if the ions were moving in separate batches of solvent; the last two terms in (4.13.12) are due to deviations from a random arrangement, which affect the combined resistance. The reason for the first order effect, proportional to $(\rho_1 - \rho_2)^2$, is that the anions in the neighborhood of a given anion are partly replaced by cations, and vice versa near cations. If anions and cations are subject to the same frictional force, that is when $\rho_1 = \rho_2$, the replacement does not matter. However, when one species of ions is more mobile than the other, then the sluggish ions will move in a countercurrent (consider the first term in (4.13.9)), while the mobile ions will be aided by a motion of their environment, whereby

$$n_1\Delta\mathbf{v}_1 + n_2\Delta\mathbf{v}_2 = 0.$$

The compensation of the corresponding forces is incomplete; hence the first order term in (4.13.12). The second-order (last) term depends simply on an overall reduction of the mean distances between the ions in the sense that the distances between ions of opposite sign are reduced more than the distances between ions of the same sign are increased. This effect always decreases the resistance to diffusion; we here meet for the first time a case where the *Coulomb forces between the ions aid a transport process*.

We obtain the equation for diffusion in the form (4.12.3) by solving (4.13.12) for \mathbf{v} and multiplying by n . Within the limits of accuracy of our calculations we may neglect second and higher powers of the corrections $\Delta\mathbf{v}_1$ and $\Delta\mathbf{v}_2$ due to Coulomb forces between the ions, which gives

$$\mathbf{J} = n\mathbf{v} = -\Omega \text{ grad } \mu = -\left(\frac{n\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} + \Delta\Omega\right) \text{ grad } \mu, \quad (4.13.13a)$$

where

$$\Delta\Omega = -\left(\frac{\omega_1 - \omega_2}{\nu_1\omega_2 + \nu_2\omega_1}\right)^2 \frac{\nu_1\nu_2}{\nu_1 + \nu_2} \frac{\kappa n}{6\pi\eta(1 + \kappa a)} + \frac{(\nu_1\omega_1 + \nu_2\omega_2)^2}{(\nu_1 + \nu_2)^2 (\nu_1\omega_2 + \nu_2\omega_1)^2} \frac{\kappa^4 \varphi(\kappa a)}{48 \pi^2 \eta}. \quad (4.13.13b)$$

In converting this formula to macroscopic units, we must remember that

$$n = N \bar{n}; \quad N\mu = \bar{\mu},$$

where N is Avogadro's number, \bar{n} the concentration in g.mols/cm³, and $\bar{\mu}$ the chemical potential in ergs/g.mol.; hence

$$\bar{\mathbf{J}} = \bar{n}\mathbf{v} = -(\Omega/N^2) \text{ grad } \mu = \bar{\Omega} \text{ grad } \bar{\mu}.$$

Substituting (3.8.40), we find

$$\bar{\Omega} = \frac{10^{-7} \bar{n}}{F^2} \frac{\Lambda_1 \Lambda_2}{\nu_1 z_1 (\Lambda_1 + \Lambda_2)} + \Delta\bar{\Omega}' + \Delta\bar{\Omega}'', \quad (4.13.15)$$

where $F = 96500$ coulomb and the first and second order correction terms are, respectively,

$$\Delta\bar{\Omega}' = -\left(\frac{z_2 \Lambda_1 - z_1 \Lambda_2}{\Lambda_1 + \Lambda_2}\right)^2 \frac{1}{z_1 z_2 (\nu_1 + \nu_2) N} \frac{\kappa \bar{n}}{6\pi\eta(1 + \kappa a)}, \quad (4.13.15a)$$

$$\Delta\bar{\Omega}'' = \left(\frac{z_2^2 \Lambda_1 + z_1^2 \Lambda_2}{\Lambda_1 + \Lambda_2}\right)^2 N^2 \epsilon^4 \frac{(\bar{n})^2}{3\eta(DRT)^2} \varphi(\kappa a). \quad (4.13.15b)$$

We are still retaining the abbreviation

$$\kappa = N\epsilon \sqrt{\frac{4\pi}{DRT} z_1 z_2 (\nu_1 + \nu_2) \bar{n}}.$$

When we introduce the values given by Birge¹ for the universal constants and write $\Lambda_1 + \Lambda_2 = \Lambda$, $1000 \bar{n} = m$ (g.mols/l.), we obtain

$$\bar{\Omega} = 1.074 \times 10^{-20} \frac{\Lambda_1 \Lambda_2}{\nu_1 z_1 \Lambda} m + \Delta\bar{\Omega}' + \Delta\bar{\Omega}'', \quad (4.13.16a)$$

$$\Delta\bar{\Omega}' = -\frac{(z_2 \Lambda_1 - z_1 \Lambda_2)^2}{\Lambda^2 z_1 z_2 (\nu_1 + \nu_2)} \frac{3.111 \times 10^{-10} m \sqrt{\Gamma}}{\eta \sqrt{DT}} \frac{1}{1 + \kappa a}, \quad (4.13.16b)$$

$$\Delta\bar{\Omega}'' = \frac{(z_2^2 \Lambda_1 + z_1^2 \Lambda_2)^2}{\Lambda^2} \frac{9.18 \times 10^{-18}}{\eta (DT)^2} m^2 \varphi(\kappa a), \quad (4.13.16c)$$

$$\kappa = \frac{3.556 \times 10^9}{\sqrt{DT}} \sqrt{z_1 z_2 (\nu_1 + \nu_2) m} = \frac{3.556 \times 10^4}{\sqrt{DT}} \sqrt{\Gamma}. \quad (4.13.16d)$$

¹ Birge: Phys. Rev. Supp., 1, 1 (1929).

Here the function $\varphi(\kappa a)$ is given by (4.13.10), and a is the mean diameter (least distance of approach) of anion and cation. For water as a solvent at 18°C we have $T = 291.2$; $D = 81.1$; $\eta = 0.01055$; hence

$$\Delta\bar{\Omega}' = - \frac{(z_2\Lambda_1 - z_1\Lambda_2)^2}{\Lambda^2} \times 19.2 \times 10^{-20} \frac{m^2}{\sqrt{\Gamma} (1 + A\sqrt{\Gamma})}, \quad (4.13.17)$$

$$\Delta\bar{\Omega}'' = \frac{(z_2^2\Lambda_1 + z_1^2\Lambda_2)^2}{\Lambda^2} \times 15.6 \times 10^{-20} m^2 \varphi(A\sqrt{\Gamma}),$$

$$A = 0.232 \times 10^8 a, \quad \Gamma = z_1 z_2 (\nu_1 + \nu_2) m,$$

and for a univalent binary electrolyte

$$10^{20}\bar{\Omega}/m = 1.074 \Lambda_1\Lambda_2/\Lambda - 9.60 \left(\frac{\Lambda_1 - \Lambda_2}{\Lambda_1 + \Lambda_2} \right)^2 \frac{\sqrt{2m}}{1 + A\sqrt{2m}} + 15.6m\varphi(A\sqrt{2m}). \quad (4.13.18)$$

The coefficient of diffusion (in c. g. s. units) is

$$D = \bar{\Omega} d\mu/d\bar{n} = 10^3 \bar{\Omega} d\mu/dm.$$

For a binary electrolyte

$$m d\mu/dm = 2 RT (1 + m d \log f/dm),$$

where f is the appropriate activity coefficient; hence at 18°C

$$D = 4.842 \times 10^{10} (\bar{\Omega}/m) (1 + m d \log f/dm). \quad (4.13.19)$$

A useful semi-empirical formula for f has been given by Hückel¹ namely

$$\log f = \frac{-0.820 \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma, \quad (4.13.20)$$

where $A\sqrt{\Gamma} = \kappa a$, applicable to strong uni-univalent electrolytes in aqueous solution at 25°. Differentiating this formula we obtain

$$1 + m d \log f/dm = 1 - \frac{0.410 \sqrt{2m}}{(1 + A\sqrt{2m})^2} + 2Bm. \quad (4.13.21)$$

On the basis of our computations, the factor $1 + md \log f/dm$ should be responsible for the variation of the diffusion coefficient of D with concentration, and we may expect that D will assume a minimum value at some concentration in the range 0.1-1*N.*, say, corresponding to the minimum of (4.13.21).

For an experimental test of our predictions, direct measurements of the differential coefficient of diffusions are preferable. Such measurements have been carried out in relatively recent times by B. W. Clack² who employed an interferometric method. Most experimenters have been content to measure the rate at which a given solution diffuses against pure solvent; this procedure

¹ Hückel: *Physik. Z.*, **26**, 93 (1925). Formulas (100) together with (27a) and (30), the latter for conversion of concentrations.

² B. W. Clack: *Proc. Phys. Soc. London*, **36**, 313 (1929).

yields a sort of an average coefficient of diffusion for all intermediate concentrations, and the type of averaging depends on the time when the experiment is interrupted for analysis. We have compared some of Öholm's data¹ with appropriate averages of our calculated D values. His results carry some resemblance to the theoretical predictions, but in several cases (KCl, NaCl), an extrapolation of his data leads to a limiting D value which is definitely higher than that computed from electrolytic mobilities, and we do not know how to interpret this discrepancy. We might mention in this connection that Öholm's measurements were performed at temperatures ranging all the way from 4°C. up to 18°, and were reduced to 18° by temperature coefficients. However, it is our impression that the discrepancy in extrapolation cannot be ascribed to an error in the temperature coefficients, because at higher concentrations Öholm's values agree substantially with those given by Clack. In the particular case of HCl, Öholm's D values extrapolate "correctly" and conform to the theory over a range of concentrations from 0.003 *n.* to 0.06 *n.* but it is not fair to select the most favorable case. We shall be content to state that reasonable inference from Öholm's data, to the extent that we have studied them, does not alter the picture which we shall presently derive from Clack's observations.

Clack measured the coefficients of diffusion for NaCl, KCl and KNO₃ over a range of concentration from 0.05 *n.* to saturation. While a lowest concentration of 0.05 *n.* does not permit a test of our "limiting laws," our calculations show that the Coulomb forces ought not (greatly) affect Ω/m very much at any concentration, which justifies a consideration of experimental data even for relatively concentrated solutions. For NaCl and KCl, but not for KNO₃, accurate measurements of the thermodynamic potentials by e.m.f. are available. Harned² found that his data could be represented very well by Hückel's formula (4.13.20); the following values for the constants A and B were derived from his data:

$$\begin{aligned}\text{NaCl: } A &= 0.84; B = 0.129; a = 3.62 \times 10^{-8} \text{ cm.} \\ \text{KCl: } A &= 0.76; B = 0.071; a = 3.28 \times 10^{-8} \text{ cm.}\end{aligned}\quad (4.13.22)$$

These values are valid for 25°, while Clack's diffusion experiments were made at 18°; the difference, which can be estimated from heats of dilution³ is negligible for our purposes. For the calculation of Ω/m , the values of A given by Harned were adopted; hence for KCl

$$10^{20} \Omega/m = 34.84 + 15.6 m \varphi(0.76\sqrt{m})$$

and for NaCl

$$10^{22} \Omega/m = 28.01 - 0.39 \frac{\sqrt{2m}}{1 + 0.84\sqrt{2m}} + 15.6 m \varphi(0.84\sqrt{2m}).$$

The results of these calculations are represented in Fig. 7. The curve for KCl is simply a graph of the function $\varphi(\kappa a)$. In Fig. 8, the solid curves are the calculated values for the coefficient of diffusion (in units cm²/sec.), while circles

¹ Öholm; *Z. physik. Chem.*, **50**, 309 (1904); **70**, 378 (1910).

² Harned; *J. Am. Chem. Soc.*, **51**, 416 (1929).

³ Wüst and Lange; *Z. physik. Chem.*, **116**, 161 (1924).

and crosses indicate different runs in Clack's experiments. The general type of the relation between D and concentration is accounted for by the theory, and for the lowest concentrations the agreement between theory and experiment is satisfactory. As regards the theoretical predictions for the variation of Ω/m with concentration, the confirmation is only negative, that is, the experiments show that for low concentrations, Ω/m does not vary much more than predicted by the theory.

At higher concentrations, we meet with quite appreciable deviations, particularly in the case of NaCl, and our theory for Ω/m is definitely not adequate.

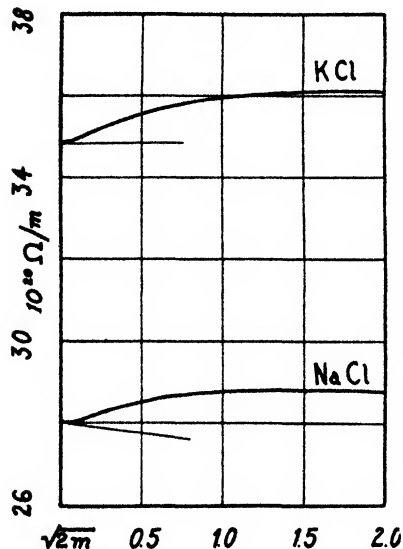


FIG. 7

Dependence of Mobility Ω/m on Concentration

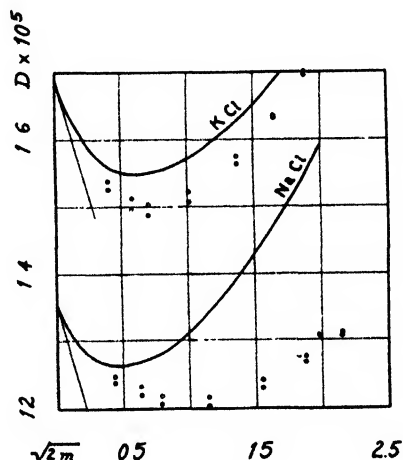


FIG. 8

Dependence of Coefficient of Diffusion on Concentration

The discrepancy is too large to be ascribed to Coulomb forces between the ions; while our calculations are admittedly not accurate for concentrated solutions, at least the order of magnitude of the effects due to these forces should be correctly computed. The differences between calculated and observed values for D are nearly linear functions of m , indicating that they are probably due to specific properties of the electrolytes, which have not been allowed for in the calculations. We suspect two effects, namely viscosity and "hydration." At 1 n. concentration, the difference (calc. — obs.) amounts to 3.4% (of calc.) in the case of KCl, and 12.5% in the case of NaCl. The fluidity of 1 n. KCl is 1.018, that of 1 n. NaCl is 0.921, reckoned to unity for pure solvent.¹

If the mobility is assumed proportional to the first power of fluidity, we obtain residual defects in D of around 5.2% for KCl and 4.6% for NaCl (at

¹ These figures are computed from macroscopic viscosities, which contain an electrostatic contribution that should actually be subtracted in calculating the "microscopic" viscosity that applies to ions; but the difference is too small to be important here.

1 n. concentration); this defect must be attributed to other causes, e.g. hydration. A fractional power of the fluidity may be more appropriate;¹ in that event, the residual effect for KCl becomes smaller, that for NaCl greater.

In using the term "hydration," we shall not necessarily imply that a given ion has a definite number of solvent molecules firmly attached, but merely that there exists a region surrounding each ion, in which other ions are relatively scarce. For a simplified picture we might assume a "forbidden" region around each ion. We have tried to estimate the "forbidden" volume from the values of A and B in (4.13.22), and obtained values of the order 10^{-22} cm³, which corresponds to a few (3) molecules of solvent. A hydration of one molecule of solvent per ion, firmly bound, (or maybe a couple loosely bound), would decrease Ω/m by 3.6%, (that is $100 \times 2 \times 18.03/1000$) at 1 n. concentration. On this basis it seems quite plausible that defects of the order 5%, as found above, can be attributed to hydration. At the same time, it becomes apparent that an exact computation would require an exceedingly detailed knowledge of concentrated electrolytes.

4.14. *The Dissipation-Function for a Simple Electrolyte.*

So far, we have consistently sought formulas which gave the velocities of the ions explicitly by the forces. For certain purposes, particularly for a simple formulation of the laws for combined conduction and diffusion, it is more convenient to express the "forces" by the velocities, as follows:

$$-\text{grad } \mu_j = \mathbf{k}_j = \sum_{\sigma=1}^s R_{j\sigma} \mathbf{J}_\sigma \quad (4.14.1)$$

In the limit of very low concentrations, only the friction of the solvent need be considered, so that

$$\mathbf{k}_j = \rho_j \mathbf{v}_j = \mathbf{v}_j / \omega_j = \mathbf{J}_j / n_j \omega_j. \quad (4.14.2)$$

At finite concentrations, the electrostatic interaction of the ions must be taken into account; hence

$$\mathbf{k}_j = \rho_j \mathbf{v}_j - e_j \Delta X_j - \rho_j \Delta \mathbf{v}_j, \quad (4.14.3)$$

where ΔX_j is the electric field on an ion due to its atmosphere, and $\Delta \mathbf{v}_j$ is the electrophoretic flow of the medium surrounding an ion, which adds $-\Delta \mathbf{v}_j$ to the relative velocity of the ion with respect to the surrounding solution.

For the case of a simple electrolyte ($s = 2$), it is possible to derive fairly simple explicit formulas, as we have in effect done above. In order to calculate the ionic field, we start conveniently with the general formula

$$-\Delta X_j = \text{grad } \psi', (o) = \frac{1}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \sqrt{n_\sigma\omega_\sigma} e_\sigma \mathbf{k}_\sigma, \quad (4.6.4)$$

(summation-sign omitted). The symmetrical matrix $\kappa.1 - K^{1/2}$ may be expanded in terms of its eigenvectors:

$$(\kappa - K^{1/2})_{ji} = \sum_{\sigma=1}^s (\kappa - \sqrt{\alpha_\sigma}) l_{\sigma j} l_{\sigma i}, \quad (4.14.4)$$

¹ This suggestion has been made by other authors for the interpretation of data on conductance.

where $\alpha_1, \dots, \alpha_s$ are the eigenvalues, and l_1, \dots, l_s the corresponding eigenvectors of K . We have shown (§ 3.8) that for our matrix K always

$$\kappa^2 = \alpha_1 > \alpha_2 \geq \dots \geq \alpha_s > 0, \quad (3.8.4)$$

$$l_{1j} = e_j \sqrt{n_j \rho_j / n_\sigma e_\sigma^2 \rho_\sigma}. \quad (3.8.5)$$

For $s = 2$, we obtain simply

$$(\kappa - K^{1/2})_{ji} = (\kappa - \sqrt{\alpha_2}) l_{2j} l_{2i}. \quad (4.14.5)$$

For this particular case (2 dimensions) an orthogonal matrix (l_{ik}) represents a rotation in the plane and has the form

$$\begin{pmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{pmatrix},$$

so that

$$\begin{aligned} l_{21} &= -l_{12} = -e_2 \sqrt{n_2 \omega_1 / (n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1)} \\ l_{22} &= l_{11} = e_1 \sqrt{n_1 \omega_2 / (n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1)}. \end{aligned} \quad (4.14.6)$$

We have also seen that for the case $s = 2$,

$$\alpha_2 = q \kappa^2 = \frac{n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2}{(n_1 e_1^2 + n_2 e_2^2) (\omega_1 + \omega_2)} \kappa^2. \quad (3.8.29)$$

Substituting these formulas in (4.6.4), we obtain

$$\Delta X = \Delta X_1 = \Delta X_2 = \frac{\kappa(1 - \sqrt{q})}{3 D k T} \frac{e_1 e_2 (n_2 e_2)}{n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1} (\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1). \quad (4.14.7)$$

We note again that ΔX is proportional to \sqrt{n} (with κ), where n is the concentration. From its derivation, (4.14.7), like our other main results, expresses an asymptotic law, and powers of n higher than $n^{1/2}$ have been neglected. In calculating this "first order" term, we may substitute the "zero order" approximation (4.14.2) for \mathbf{k}_1 and \mathbf{k}_2 , as follows:

$$n_2 e_2 (\omega_2 \mathbf{k}_2 - \omega_1 \mathbf{k}_1) = n_2 e_2 (\mathbf{v}_2 - \mathbf{v}_1) = n_2 e_2 \mathbf{v}_2 + n_1 e_1 \mathbf{v}_1 = e_1 \mathbf{J}_1 + e_2 \mathbf{J}_2. \quad (4.14.8)$$

It is seen that the ionic field ΔX is proportional to the velocity difference between anions and cations.

The electrophoretic correction we take from (4.2.15), omitting the "second order" term with $\varphi(\kappa a)$; thus

$$n_j \Delta \mathbf{v}_j = - \frac{2}{3 \eta \kappa D k T} n_j e_j \sum n_\sigma e_\sigma \mathbf{k}_\sigma$$

or, with the approximation (4.14.2) for \mathbf{k}_1 and \mathbf{k}_2 :

$$- \rho_j \Delta \mathbf{v}_j = \frac{2}{3 \eta \kappa D k T} e_j \rho_j \sum e_\sigma \rho_\sigma \mathbf{J}_\sigma. \quad (4.14.9)$$

We substitute this formula together with (4.14.7-8) in (4.14.3), and obtain

$$\begin{aligned} \mathbf{k}_j &= \frac{\rho_j}{n_j} \mathbf{J}_j + \frac{\kappa}{3 D k T} \frac{(-e_1 e_2) (1 - \sqrt{q})}{(n_1 e_1^2 \omega_2 + n_2 e_2^2 \omega_1)} e_j (e_1 \mathbf{J}_1 + e_2 \mathbf{J}_2) \\ &\quad + \frac{2}{3 \eta \kappa D k T} e_j \rho_j (e_1 \rho_1 \mathbf{J}_1 + e_2 \rho_2 \mathbf{J}_2). \end{aligned} \quad (4.14.10)$$

By comparison with (4.14.1) it is seen that the reciprocal relation

$$R_{12} = R_{21}$$

holds. We may then write (4.14.10) in the form

$$\mathbf{k}_j = \partial F / \partial \mathbf{J}_j, \quad (4.14.11)$$

with the *dissipation-function*

$$\begin{aligned} 2F = R_{11}\mathbf{J}_1^2 + 2R_{12}\mathbf{J}_1\mathbf{J}_2 + R_{22}\mathbf{J}_2^2 = & (\mathbf{J}_1^2/n_1\omega_1) + (\mathbf{J}_2^2/n_2\omega_2) \\ & + \frac{-e_1e_2\kappa}{3DkT} \frac{(1 - \sqrt{q})}{(n_1e_1^2\omega_2 + n_2e_2^2\omega_1)} (e_1\mathbf{J}_1 + e_2\mathbf{J}_2)^2 + \\ & \frac{2}{3\eta\kappa DkT} (e_1\rho_1\mathbf{J}_1 + e_2\rho_2\mathbf{J}_2)^2. \end{aligned} \quad (4.14.12)$$

The ionic field and the electrophoresis both cause positive contributions to the dissipation-function. The former vanishes when all ions migrate with the same velocity, which in the case of a simple electrolyte means no electric current. The additional dissipation due to electrophoresis vanishes when

$$e_1\mathbf{J}_1\rho_1 + e_2\rho_2\mathbf{J}_2 = n_1e_1(\mathbf{v}_1\rho_1 - \mathbf{v}_2\rho_2) = 0,$$

that is, when anions and cations meet the same frictional resistance per ion, (both migrating in the same direction).

When the theory is elaborated to include in the dissipation-function terms of higher order than \sqrt{n} for instance $n \log n$, the picture becomes more complicated. While we have made no exhaustive search for terms of any order higher than the first, we may point out that the second order term in formula (4.2.15) for the electrophoretic effect will lead to the *negative* term

$$- \frac{\varphi(\kappa a)}{3\eta(DkT)^2} (e_1^2\rho_1\mathbf{J}_1 + e_2^2\rho_2\mathbf{J}_2)_z$$

in the dissipation-function.

4.15. Diffusion of a General Electrolyte.

Dissipation-function.

Diffusion in a system containing three or more ions is a subject of considerable interest. The case which has received the most attention is the interdiffusion of two different electrolytes; both the rates of diffusion and, particularly, the electromotive forces at the boundary have been studied. Unfortunately, the equations of diffusion for such cases are very difficult to integrate even when the variation of activity coefficients and mobilities with concentration is neglected. The velocities of the ions 1, . . . , s are determined by the gradients of concentration, $n_1 \dots n_s$, subject to the condition of electric neutrality

$$\sum_i n_i e_i = 0, \quad (4.15.1)$$

and by the electric field; the latter automatically adjusts itself so that the solution remains electrically neutral everywhere in accord with (4.15.1).

When the effects of Coulomb forces between the ions are neglected, (except the macroscopic electric field, which depends on space charges in the electrolyte), the equations of diffusion are for a one-dimensional case (parallel flow)

$$\mathbf{J}_i = \omega_i n_i e_i \mathbf{X} - kT \partial n_i / \partial x \quad (4.15.2)$$

together with (4.15.1). The electric field is related to the current density

$$\mathbf{i} = \sum_i e_i \mathbf{J}_i$$

by the equation

$$\lambda \mathbf{X} = \mathbf{i} + kT \sum_i e_i \omega_i \partial n_i / \partial x, \quad (4.15.3)$$

where λ denotes the specific conductance of the solution:

$$\lambda = \sum_i n_i e_i^2 \omega_i.$$

The integration on (4.15.2) and (4.15.3) cannot be carried out in closed form except in certain special cases, most of which are trivial. The one case of interest which can be conveniently computed is the interdiffusion of two electrolytes (mixtures) of nearly the same composition,¹ determined by the differential coefficients of diffusion for the given (nearly constant) composition. The computation of this special case is feasible because $n_1 \dots n_s$ may be considered (for a first approximation) as constant coefficients in a system of equations involving $\partial n_1 / \partial x, \dots, \partial n_s / \partial x$, linear in the latter. If necessary, the variation of $n_1 \dots n_s$ may be taken into account by successive approximations.

The simple theory demands that the differential coefficients of diffusion should depend only on the *ratios* of $n_1 \dots n_s$ and remain constant when the concentrations are varied in proportion. When the interionic forces are taken into account, this simple relation no longer holds; our object is to calculate the corrections.

We shall develop differential equations which allow for the Coulomb forces between the ions, and discuss the most important relations to the underlying physical picture. For eventual applications, it would be necessary to integrate our final equations, which is again feasible for the case of *differential* diffusion, as outlined above. As long as no actual measurements of this type are available, we have not found it worth labor and space to carry out these integrations.

We employ the general form (4.12.8)

$$\mathbf{k}_i = - \text{grad } \mu_i = \sum_{k=1}^s R_{ik} \mathbf{J}_k, \quad (4.15.4)$$

with the convention (4.12.15), that the electric field \mathbf{X} is included in $\text{grad } \mu$, thus:

$$- \text{grad } \mu_i = - \text{grad } \mu_i' + e_i \mathbf{X}.$$

The splitting of $\text{grad } \mu_i$ into an electrical part $e_i \mathbf{X}$ and a "chemical" part $\text{grad } \mu_i'$ has been discussed in § 4.12. As shown there, the concentration

¹ For example, one solution containing KCl (0.050 *N*) and HCl (0.030 *N*), and another containing KCl (0.050 *N*) and HCl (0.028 *N*).

gradients yield $n-1$ relations to determine $\text{grad } \mu_1, \dots, \text{grad } \mu_n$; the n th relation necessary to complete the determination is derived from the condition of electric neutrality (4.15.1), which again leads to

$$\sum e_i \partial n_i / \partial t = - \text{div } \sum e_i \mathbf{J}_i = - \text{div } \mathbf{i} = 0,$$

or in the case of parallel flow:

$$-\sum_i e_i \sum_k \Omega_{ik} \partial \mu_k / \partial x = \sum_i e_i \mathbf{J}_i = \mathbf{i} = \text{const.} \quad (4.15.5)$$

where \mathbf{i} is the electric current.

The case of "pure diffusion" is defined by $\mathbf{i} = 0$, for our purposes a specialization of no important consequence, except that it is common in practice.

We employ the general formula (4.14.3)

$$\mathbf{k}_j = \rho_j \mathbf{v}_j - e_j \Delta \mathbf{X}_j - \rho_j \Delta \mathbf{v}_j, \quad (4.15.6)$$

where the terms on the right represent, in the order named, the friction of the ion against the solvent, the asymmetric electric field of the atmosphere, and the electrophoretic velocity at the centre of the atmosphere. We can calculate the latter as in the preceding section (4.14.9), thus

$$-\rho_j \Delta \mathbf{v}_j = \frac{2}{3\eta\kappa DkT} e_j \rho_j \sum_{\sigma} e_{\sigma} \rho_{\sigma} \mathbf{J}_{\sigma} = R'_{j\sigma} \mathbf{J}_{\sigma}. \quad (4.15.7)$$

For the ionic field, we use the formula

$$\begin{aligned} -\Delta X_j &= \text{grad } \psi'_j(0) = \\ &= \frac{1}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \sqrt{n_{\sigma}\omega_{\sigma}} e_{\sigma} \mathbf{k}_{\sigma}, \end{aligned} \quad (4.6.4),$$

or, substituting the "zero approximation"

$$\mathbf{k}_i = \mathbf{v}_i / \omega_i = \mathbf{J}_i / n_i \omega_i$$

for the force,

$$-e_j \Delta X_j = \frac{e_j}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \frac{e_{\sigma}}{\sqrt{n_{\sigma}\omega_{\sigma}}} \mathbf{J}_{\sigma} = R''_{j\sigma} \mathbf{J}_{\sigma}. \quad (4.15.8)$$

Now if we write

$$R_{ji} = (\rho_j / n_j) \delta_{ji} + R'_{ji} + R''_{ji}$$

where R'_{ji} and R''_{ji} are given by (4.15.7-8), we have from (4.15.6)

$$\mathbf{k}_j = R_{j\sigma} \mathbf{J}_{\sigma} = (\rho_j / n_j) \mathbf{J}_j + (R'_{j\sigma} + R''_{j\sigma}) \mathbf{J}_{\sigma}. \quad (4.15.9)$$

Here we shall point out in the first place that the matrix R is symmetrical, as required by (4.12.9). The first term in (4.15.9) is diagonal; R'_{ji} is symmetrical according to (4.15.7), and R''_{ji} likewise according to (4.15.8), on account of the symmetry of the matrix K .

The dissipation function takes the form

$$\begin{aligned}
 {}_2 F(\mathbf{J}, \mathbf{J}) &= \sum R_{ji} \mathbf{J}_j \mathbf{J}_j = \\
 &= \sum \frac{\rho_j}{n_j} \mathbf{J}_j^2 + \frac{2}{3\eta\kappa DkT} (\sum e_j \rho_j \mathbf{J}_j)^2 + \frac{1}{3DkT} \left(\sum_j \frac{e_j^2 \kappa}{n_j \omega_j} \mathbf{J}_j^2 - \sum_{j,i} \frac{K^{1/2} e_j e_i}{\sqrt{n_j n_i \omega_j \omega_i}} \mathbf{J}_j \mathbf{J}_i \right)
 \end{aligned} \quad (4.15.10)$$

The fundamental equations for combined conduction and diffusion are

$$- \text{grad } \mu_i = \partial F / \partial \mathbf{J}_i = \sum_k R_{ik} \mathbf{J}_k. \quad (4.15.11)$$

In the dissipation-function (4.15.10), the electrophoretic contribution (second term) consists of a single squared term. The contribution from the ionic fields ${}_2 F'' = \sum R''_{ji} \mathbf{J}_j \mathbf{J}_i$ contains $s-1$ squared terms, which is the number of positive characteristic numbers of the quadratic form

$$\kappa \sum x^2 - K^{1/2} (x, x) = \sum_{p=1}^s (\kappa - \sqrt{\alpha_p}) (\sum_i l_{pi} x_i)^2,$$

where according to (3.8.4),

$$\kappa^2 = \alpha_1 > \alpha_2 \geq \dots \geq \alpha > 0.$$

This implies that F'' will vanish for a certain not trivial set of values of $\mathbf{J}_1, \dots, \mathbf{J}_s$, corresponding to the eigenvector l_i of \mathbf{K} . From (3.8.5), it is easily verified that F'' vanishes when

$$\mathbf{J}_1/n_1 = \mathbf{J}_2/n_2 = \dots = \mathbf{J}_s/n_s = \mathbf{v}_1 = \mathbf{v}_2 = \dots = \mathbf{v}_s,$$

that is, when the velocities of all ions are equal. This is what we should expect, because a simultaneous displacement of all ions will not disturb the ionic atmospheres. We may, therefore, if we like, express F'' in the alternative form

$${}_2 F'' = -\frac{1}{2} \sum_{j,i} R''_{ji} n_j n_i (\mathbf{v}_j - \mathbf{v}_i)^2, \quad (4.15.12)$$

which is the same as $\sum_{j,i} R''_{ji} \mathbf{J}_j \mathbf{J}_i$ because, as is readily verified with the aid of (3.8.5)

$$\sum_i n_i R''_{ji} = \sum_i n_i R''_{ij} = 0.$$

The construction of the electrophoretic term F' in (4.15.10) is apparent on sight; but some interesting properties of F'' are hidden. We shall next show that F'' , the contribution to the dissipation function arising from the interaction of the ionic fields, is proportional to the $3/2$ power of the total ionic strength Γ and that the proportionality factor is determined by the velocities $\mathbf{v}_1, \dots, \mathbf{v}_s$, the mobilities $\omega_1, \dots, \omega_s$, and the ratios of ionic strengths μ_1, \dots, μ_s . We have for ${}_2 F''$, according to (4.5.10),

$$\begin{aligned}
 {}_2 F'' &= \sum_{j,i} R''_{ji} \mathbf{J}_j \mathbf{J}_i = \mathbf{J}_\sigma R''_{\sigma\tau} \mathbf{J}_\tau = \\
 &= \frac{\kappa}{3DkT} \sqrt{n_\sigma \rho_\sigma e_\sigma v_\sigma} (1 - \kappa^{-1} K^{1/2})_{\sigma\tau} \sqrt{n_\tau \rho_\tau e_\tau v_\tau}.
 \end{aligned} \quad (4.15.13)$$

We now recall the transformation (4.7.5):

$$M^{-1} f(\kappa^2 K) M = \kappa^{-2} f(G) = f(H), \quad m_{ji} = \delta_{ji} e_j \sqrt{n_j \omega_j} \quad (4.7.5)$$

$$h_{ji} = \delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_i \frac{\omega_i}{\omega_i + \omega_j} \quad (4.7.7)$$

by means of which we introduced a matrix H where the elements are all pure numbers. On applying (4.7.5) to (4.15.13), we obtain

$${}_2F'' = \frac{\kappa}{3DkT} n_\sigma e_\sigma^2 \nabla_\sigma (1 - H^{1/2})_{\sigma\tau} \nabla_\tau \rho_\tau$$

and on substituting (4.7.1-3),

$${}_2F'' = \left(\frac{N e^2}{1000 k} \right)^{3/2} \frac{2\sqrt{\pi}}{3} \left(\frac{\Gamma}{DT} \right)^{3/2} \mu_\sigma \nabla_\sigma (1 - H^{1/2})_{\sigma\tau} \nabla_\tau \rho_\tau. \quad (4.15.14)$$

Numerical computation by means of (4.15.14) is made by a procedure parallel to that developed in § 4.7 for the conductance problem; there is no need to repeat the manipulation here. In (4.15.14), the concentrations of the various ionic species appear only as the ratios $\mu_j = \Gamma_j/\Gamma$, while the total concentration is represented by the factor $\Gamma^{3/2} = (m_\sigma z_\sigma^2)^{3/2}$. The mobilities enter in the elements of H , by their ratios, (cf. 4.7.7), and in the vector with components $\nabla_j \rho_j$ representing the force on an ion.

It is of interest to compute the dissipation function for a special case, corresponding to equal mobilities

$$\omega_1 = \omega_2 \dots = \omega_s = \omega = 1/\rho,$$

because the nature of the various terms of (4.15.10) is then very readily seen. For this case, the term ${}_2F''$ simplifies to

$${}_2F'' = \frac{\kappa\rho}{3DkT} \sqrt{n_\sigma} e_\sigma \nabla_\sigma (1 - \kappa^{-1} K^{1/2})_{\sigma\tau} \sqrt{n_\tau} e_\tau \nabla_\tau,$$

which may be written in terms of a quadratic form $C(x, x)$,

$${}_2F'' = \frac{\kappa\rho}{3DkT} C(\sqrt{n} e \nabla, \sqrt{n} e \nabla). \quad (4.15.15)$$

The form $C(x, x)$ is easily determined because the elements of $\kappa^{-2}K$ reduced to

$$\kappa^{-2} k_{ji} = \frac{1}{2} \delta_{ji} + \frac{e_i e_j \sqrt{n_i n_j}}{2 n_\sigma e_\sigma^2}.$$

The second term contains only the eigenvector l_1 (cf. (3.8.5)), thus

$$\kappa^{-2} k_{ji} = \frac{1}{2} \delta_{ji} + \frac{1}{2} l_{1j} l_{1i}.$$

Then we have for the quadratic form $K(x, x)$ in this special case

$$K(x, x) = \kappa^2 (l_{1\sigma} x_\sigma)^2 + \sum_{p=0}^i \frac{1}{2} \kappa^2 (l_{p\sigma} x_\sigma)^2,$$

so that the characteristic numbers are

$$\alpha_1 = \kappa^2, \alpha_2 = \alpha_3 = \dots = \alpha_s = \kappa^2/2.$$

Then $C = (1 - \kappa^{-1} K^{1/2})$ has the same eigenvectors and the characteristic numbers

$$\xi_1 = 0, \xi_2 = \xi_3 = \dots = \xi_s = 1 - \sqrt{1/2} = (2 - \sqrt{2})/2$$

and

$$C(x, x) = \frac{2 - \sqrt{2}}{2} (x_\sigma^2 - (l_{1\sigma} x_\sigma)^2). \quad (4.15.16)$$

Substituting (4.15.16) in (4.15.15), we obtain

$$\begin{aligned} {}_2F'' &= \frac{\kappa\rho(2 - \sqrt{2})}{6DkT} \left\{ \sum_i n_i e_i^2 \mathbf{v}_i^2 - \left(\frac{\sum_i \sqrt{n_i} e_i \sqrt{n_i} e_i \mathbf{v}_i}{(\sum_k n_k e_k^2)^{1/2}} \right)^2 \right\} \quad (4.15.17) \\ &= \frac{2 - \sqrt{2}}{6} \frac{\kappa\rho}{DkT} \sum_i n_i e_i^2 (\mathbf{v}_i - \bar{\mathbf{v}})^2, \end{aligned}$$

where

$$\bar{\mathbf{v}} = n_\sigma e_\sigma^2 \mathbf{v}_\sigma / n_\tau e_\tau^2$$

denotes the average velocity of the atmosphere. Hence, when the coefficients of diffusion, (kT/ω) are the same for all ions, the entire dissipation-function takes the form

$$\begin{aligned} {}_2F(\mathbf{v}, \mathbf{v}) &= \rho \sum_i n_i \mathbf{v}_i^2 + \frac{2\rho}{3\eta\kappa DkT} (\sum_j n_j e_j \mathbf{v}_j)^2 \\ &+ \frac{2 - \sqrt{2}}{6} \frac{\kappa\rho}{DkT} \sum_j n_j e_j^2 (\mathbf{v}_j - \bar{\mathbf{v}})^2. \end{aligned} \quad (4.15.18)$$

The first term on the right is the contribution to entropy production (energy dissipation) due to the frictional forces of the ions against the solvent. The second term represents the contribution due to the electrophoretic effect, and is approximately independent of the viscosity of the solvent, because the ratio $\eta/\rho \sim$ ionic radius enters. (cf. (4.2.4)). The last term is the effect produced by the asymmetry of the ionic fields, and as might be suspected, depends on the differences in mobility of the various ionic species present.

5. Summary

1. The effects of the Coulomb forces between ions on *transport processes*, namely: diffusion, electrolytic conduction, and viscous flow are considered from a common point of view.

2. It is shown how results previously obtained for simple electrolytes can be extended to mixtures containing an arbitrary number of ionic species, and general limiting laws are derived. As in the case of simple electrolytes, the electrostatic effects are *proportional to the square root of concentration*.

3. The fundamental equations of the ionic atmospheres lead to systems of differential equations which are compactly treated by *matrix algebra*. The *numerical* evaluation of the formal results is illustrated by examples.

4. The electrostatic contribution to *viscosity* is computed explicitly for the general case, and some simple special cases are discussed in more detail. The mechanism of *force transfer* is investigated.

5. The general limiting laws for *conduction in mixtures* are derived. Kohlrausch's rule of the independent migration of ions, valid as a limiting law for simple binary electrolytes, does not apply to mixtures, nor are the conductances additive. The computed deviations are compared with experiment.

6. The *general laws of diffusion* are discussed with particular reference to electrolytes. The effects of the Coulomb forces are computed for simple electrolytes and for mixtures. The theoretical results for the former are compared with the available data.

7. The rate of production of entropy in transport processes is a quadratic function of the velocities. With the aid of this *dissipation-function*, the laws of combined diffusion and electric conduction are formulated and discussed.

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FLUORINE POLYHALIDES¹

BY HAROLD SIMMONS BOOTH, CARL F. SWINEHART AND WILLIAM C. MORRIS

Introduction

Many polyhalides of the various elements, chiefly of the alkali metals of the first group, have been prepared. Numerous methods have been used to prepare the polyhalides, and there is question as to whether or not some that are said to exist really do. But chemists seem to have forgotten that fluorine is a halogen; all of the studies have been made on the polyhalides containing chlorine, bromine, and iodine, in various combinations and proportions. Perhaps the reason for this apparent oversight of fluorine has been the aversion of chemists to the handling of fluorine and the fluorides.

According to Sidgwick,¹ "Any halogen except fluorine can form part of a perhalide." He assumes that fluorine does not follow the behavior peculiar to the polyhalide formation because it is the lightest halogen and only the heavier ones follow this rule.

The purpose of this paper is to describe the preparation of the salts formed by the union of iodine trichloride and the fluorides of the alkali metals, cesium, rubidium, potassium, and ammonium, their properties and the experimental data for the preparation and analyses of the salts.

Historical

It has long been known that iodine would dissolve in potassium iodide solutions, either alcoholic or aqueous, but it was not known whether it was merely a physical solution or whether a complex polyhalide of potassium was formed. There was some evidence for both lines of reasoning. Baudrimont² found that carbon disulfide removed the iodine dissolved in an aqueous solution of potassium iodide. This would indicate that no chemical compound was formed. Jorgensen³ said that carbon disulfide did not remove iodine from an alcoholic solution of potassium iodide containing two atomic weights of iodine for each atomic weight of potassium iodide. He also showed that an alcoholic solution of potassium iodide completely removed the iodine from a solution of it dissolved in carbon disulfide. This would indicate that a compound was formed by the iodine uniting with the potassium iodide.

Since this early work there have been many complex halides isolated containing not only iodine but also chlorine and bromine. All of the polyhalides

* Contribution from the Morley Chemical Laboratory, Western Reserve University. First published in part as a "Note to the Editor" *J. Am. Chem. Soc.*, **54**, 2561 (1932).

¹ Sidgwick: "The Electronic Theory of Valence," 293 (1927).

² Baudrimont: *Compt. rend.*, **51**, 825 (1860).

³ Jorgensen: *J. prakt. Chem.*, **2**, 347 (1870).

that have been prepared may be divided into two major classes; those containing three halogen atoms and those containing five halogen atoms. Table I contains a list of all of the alkali metal polyhalides, arranged in the order of increasing stability. This stability is based on the temperature to which it is necessary to heat the compound in an open tube before it whitens. In general the stability is as follows: $\text{Cs} > \text{Rb} > \text{NH}_4 > \text{K} > \text{Na} > \text{Li}$.

Trihalides

By concentrating an aqueous or alcoholic iodine-potassium iodide solution over sulfuric acid in a desiccator Johnson¹ obtained some large, dark blue, prismatic crystals which he claimed, from the result of his analyses, to be potassium triiodide. Wells² and some of his co-workers repeated Johnson's preparation but not the analysis.

Abegg and Hamburger³ attempted to determine the composition of all the alkali polyiodides that are stable at 25°C. by shaking the solid iodide in varying amounts of a nearly saturated solution of iodine in benzene. They found no evidence of the compound KI_3 . Several phase rule studies of the system $\text{KI}-\text{I}_2-\text{H}_2\text{O}$ have been made but none of them even indicated that KI_3 existed. Bancroft⁴ made a phase-rule study of the system and found no evidence for the existence of KI_3 . On repeating Johnson's work he obtained the same salt and, by using the same inaccurate method of analysis that Johnson used, he found that the iodine content of the salt corresponded with that required for KI_3 . On making an X-ray study of the salt he found that there was no indication that the salt was potassium tri-iodide. Bancroft concluded from his study of the salt that it was merely potassium iodide that had taken up enough iodine to change its crystal structure slightly and to give the analysis corresponding to KI_3 .

Briggs and Geigle⁵ made a freezing point study of various mixtures of potassium iodide and iodine and found that potassium iodide and iodine were the only solids that could exist in equilibrium with the melt.

Serullas⁶ prepared potassium dichloro-bromide and potassium dibromochloride by the action of chlorine monobromide on potassium chloride and potassium bromide. Abegg and Hamburger (loc. cit) found evidence for the existence of RbI_3 , CsI_3 , and NH_4I_3 . Foote and Chalker⁷ claim to have isolated the tri-iodides of cesium, rubidium, and potassium. Wells and Wheeler (loc. cit.) have prepared the following trihalides in addition to the potassium triiodides: CsBrI_2 , CsBr_2I , CsClBrI , CsCl_2I , CsBr_3 , CsClBr_2 , CsCl_2Br , CsI_3 , RbI_3 , RbBr_2I , RbClBrI , RbBr_3 , RbCl_2Br , RbClBr_2 , KBr_2I , and KCl_2I by dissolving the normal halide and the halogen in question in a warm water or

¹ Johnson: J. Chem. Soc., 31, 249 (1877).

² Wells: "Studies from the Chemical Laboratory, Sheffield Scientific School," Vol. I, Inorganic Chemistry.

³ Abegg and Hamburger: Z. anorg. Chem., 50, 427 (1906).

⁴ Bancroft: J. Phys. Chem., 35, 764 (1931).

⁵ Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930).

⁶ Serullas: Ann. Chim. Phys., 45, 190 (1830).

⁷ Foote and Chalker: Am. Chem. J., 39, 561 (1908).

weak alcohol solution. They were unable to prepare the other trihalides necessary to complete the series. The colors range from brilliant black for CsI_3 to bright yellow for CsCl_2Br . They found that the trihalides containing iodine were more stable than those not containing iodine, but that the instability of the compound was not governed entirely by the volatility of the halogen, for they found that CsCl_2Br was more stable than CsClBr_2 .

Several of the ammonium trihalides have been prepared. They are very similar to the alkali metal trihalides and are prepared in the same way. Johnson¹ obtained NH_4I_3 by passing ammonia gas into the mother liquor from which the potassium tri-iodide was crystallized. Besides the normal trihalide he also obtained two salts having the composition $\text{NH}_4\text{I}_{3.7}\text{KI}$ and $5\text{NH}_4\text{I}_3\cdot\text{KI}$ respectively. Roozeboom² prepared ammonium tribromide, NH_4Br_3 . Chataway³ obtained the following trihalides, $\text{NH}_4\text{Cl}_2\text{I}$, NH_4ClBrI , and NH_4Br_3 and found that the first one was the most stable.

Ray and Sarkar⁴ studied the formation of aqueous solutions of HClI_2 , HClBr_2 , and HBrI_2 by means of the distribution of halogen between an aqueous solution of the acid in question and chloroform, carbon disulfide, or benzene. They found that HBrI_2 was the most stable and that the other two were about as stable as the corresponding potassium salts. Cremer and Duncan⁵ found evidence for the existence of HIBr_2 , HICl_2 , and HIBrCl in solution.

Pentahalides of the Alkali Metals

Wells and Wheeler (loc. cit.) also prepared the following pentahalides: CsI_5 , CsBr_5 , $\text{CsCl}\cdot\text{ICl}_3$, $\text{RbCl}\cdot\text{ICl}_3$, $\text{KCl}\cdot\text{ICl}_3$, $\text{NaCl}\cdot\text{ICl}_3\cdot 2\text{H}_2\text{O}$, and $\text{LiCl}\cdot\text{ICl}_3\cdot 4\text{H}_2\text{O}$. The method of preparation is very similar to that used in the preparation of the trihalides. The first five are fairly stable while the last two are very unstable. According to Wells and Wheeler, when the pentahalides are heated they apparently lose halogen and go to the trihalide since the pentahalides all whiten at approximately the same temperature as the corresponding trihalides. On that basis are they listed in Table I.

There are some higher polyhalides described in the literature but there is some doubt about their existence. Abegg and Hamburger found evidence for the existence of KI_7 , RbI_7 , RbI_9 , CsI_7 , and CsI_9 . Foote and Chalker claimed to obtain KI_7 but none of the other polyiodides with more than five atoms of iodine.

Rae⁶ has prepared CsBr_4 and CsBr_3 and thinks that the tetrabromide was the real compound discovered by Wells and Wheeler and called pentabromide by them. By running the isothermal diagram for the system $\text{CsI} - \text{I}_2 - \text{H}_2\text{O}$, Briggs, Greenwald, and Leonard⁷ found the CsI_3 and CsI_4 but did not find any evidence for CsI_5 .

¹ Johnson: J. Chem. Soc., 33, 397 (1878).

² Roozeboom: Ber., 14, 2398 (1881).

³ Chataway: J. Chem. Soc., 107, 105 (1915).

⁴ Ray and Sarkar: J. Chem. Soc., 121, 1449-55 (1922).

⁵ Cremer and Duncan: J. Chem. Soc., 133, 1857-66 (1931).

⁶ Rae: J. Chem. Soc., 133, 1578-81 (1931).

⁷ Briggs, Greenwald, and Leonard: J. Phys. Chem., 34, 1951-50 (1930).

TABLE I

The Alkali Metal Polyhalides

(Arranged in order of increasing stability, based on the temperature at which they whiten when heated in an open tube)

Trihalides		Pentahalides	
Formula	Whiten at Degrees C	Formula	Whiten at Degrees C
RbClBr ₂	80°	NaCl.ICl ₃ .2H ₂ O	115°
RbCl ₂ Br	110°	LiCl.ICl ₃ .4H ₂ O	180°
RbBr ₃	140°		
CsClBr ₂	150°		
CsCl ₂ Br	150°		
CsBr ₃	160°	CsBr ₅	
KBr ₂ I	180°		
RbClBrI	200°		
KCl ₂ I	215°	KCl.ICl ₃	
KI ₃	225°		
CsBrI ₂	260°		
RbCl ₂ I	265°	RbCl.ICl ₃	
RbBr ₂ I	265°		
RbI ₃	270°		
CsCl ₂ I	290°	CsCl.ICl ₃	
CsClBrI	290°		
CsBr ₂ I	320°		
CsI ₃	330°	CsI ₅	

(The data on the pentahalides are uncertain)

Polyhalides containing Fluorine

At the time these studies were begun no evidence of the existence of polyhalides containing fluorine had been adduced. Cremer and Duncan¹ in studying the dissociation pressures and other properties tried the absorption of iodine bromide by cesium fluoride and found evidence for a compound having the formula CsFIBr. It should be very similar in its composition and properties to the cesium chloride-iodine-monobromide. No description or analysis was given and apparently they did not isolate the salt.

Preparation of Fluorine Polyhalides

For the preparation of the fluorine polyhalides four procedures were used. In the first method chlorine was passed into a hot saturated solution of the normal fluoride, containing one equivalent weight of iodine for each atom of fluorine, until all of the iodine color had disappeared. On cooling the solution, small orange-yellow, needle-like crystals were obtained, but these were not all

¹ Cremer and Duncan: J. Chem. Soc., 133, 2243-54 (1931).

homogeneous. By careful recrystallization this salt gave a crop of homogeneous crystals. However, this method gave a very poor yield.

The second method tried was practically the same as the first except that the solution of the fluoride was slightly acidified. This gave a much better yield and the crystals were homogeneous when examined under the microscope. In both the above methods of preparation the chlorination was accomplished in an Erlenmeyer flask of appropriate size, fitted with a reflux condenser to return both water and any volatile iodine-chloride formed. The flask was weighed before and after chlorinating and the amount of chlorine absorbed gave some idea as to the compound formed.

In the third or dry method, the normal fluoride was intimately mixed by grinding with one equivalent weight of iodine for each atom of fluorine, and then chlorinated to constant weight in a flask similar to the above with chlorine dried by concentrated sulfuric acid. A dark brown pasty liquid first appeared which gradually changed over to a bright yellow solid. The intermediate product was formed fairly rapidly and probably was a eutectic mixture of iodine monochloride and the fluoride. The final product is formed very slowly. On recrystallizing this solid, very good yields of the same bright yellow, needle-like crystals previously described were obtained. However, this method is too slow.

The fourth and best method found for the preparation of the fluorine polyhalides was to add a slight excess of a cold saturated solution of iodine trichloride to a cold, saturated, slightly acid solution of the normal fluoride. On mixing the two aqueous solutions the characteristic brilliant yellow crystals separated out immediately. After recrystallization, these were entirely homogeneous. A much better yield is obtained by this method than by any of the others.

The iodine trichloride was made by subliming iodine from a glass retort into an ice-cooled flask similar to the other chlorinating flasks while a stream of chlorine in excess of that required to form ICl_3 was sent through it. The bright yellow iodine trichloride deposits on the cold bottom and sides of the flask. This method of forming ICl_3 is much better and quicker than that of chlorinating the solid iodine to the trichloride or to constant weight.

Preparation of the Cesium Fluorine Polyhalide

Cesium chloride was converted to the fluoride by first heating it with an excess of sulfuric acid; this bisulfate was then converted to cesium hydroxide by treating the hot solution of the sulfate with a hot saturated barium hydroxide solution, which precipitated the sulfate as barium sulfate and converted the cesium into cesium hydroxide. By careful addition of the barium hydroxide solution the point was reached at which there was neither sulfate nor barium in solution. The barium sulfate was filtered off and the cesium hydroxide solution was evaporated until the cesium hydroxide or cesium carbonate began to separate. This was then neutralized with hydrofluoric acid. On mixing an aqueous solution of the iodine trichloride with a slightly acid solution of cesium fluoride, the brilliant yellow needles of the cesium polyhalides separated.

The cesium polyhalide is much more stable than the potassium salt, but it does lose halogen slowly in the open. For this reason it is best kept in tightly stoppered bottles. Analyses of this salt (Table II) shows that it has the formula CsFICl_3 .

TABLE II
Results of Analyses of Salts

				Theoretical for
<i>Cesium salt, Specimen 1</i>				CsFICl_3
Cesium (perchlorate method):		34.27%,	34.33%	34.49% Cs
<i>Cesium salt, Specimen 2</i>				
Cesium (by gentle ignition):		34.59%,	34.56%	
Average (both specimens)			34.44%	34.49% Cs
Chlorine:	27.61%, 28.06%	Average	27.84%	27.62% Cl
Iodine:	33.38%, 32.81%	"	33.09%	32.96% I
			95.37	
Fluorine by difference:			4.63%	4.93% F
				Theoretical for
<i>Rubidium salt</i>				RbFICl_3
Rubidium:	25.27%, 25.43%	Average	25.35	25.30% Rb
Chlorine:	31.46%, 31.52%	"	31.49	31.50% Cl
Iodine:	37.52%, 38.05%	"	37.78	37.58% I
			94.62	
Fluorine by difference			5.38	5.62% F
				Theoretical for
<i>Potassium salt</i>				KFICl_3
Potassium:	13.37%, 13.31%	Average	13.34	13.42% K
Chlorine:	36.60%, 36.46%	"	36.53	36.51% Cl
Iodine:	43.57%, 43.67%	"	43.62	43.75% I
			93.49	
Fluorine by difference			6.51	6.32% F
				Theoretical for
<i>Ammonium salt</i>				NH_4FICl_3
NH_3 calc. to				
NH_4F :	13.57%, 13.53%	Average	13.55%	13.68%
Chlorine:	39.39%, 39.32%	"	39.36%	39.44% Cl
Iodine:	46.79%, 46.82%	"	46.81%	46.90% I
			99.72%	

Preparation of the Rubidium Fluorine Polyhalide

Starting with rubidium chloride, the rubidium fluorine polyhalide was prepared in the same way as the cesium salt. The rubidium fluorine polyhalide is similar to the cesium salt. It is much more stable than the corresponding potassium salt but not quite as stable as the cesium salt. Analyses (Table II) show it has the formula RbFICl_3 .

Preparation of the Potassium Fluorine Polyhalide

The potassium fluoride used was obtained from the pure acid fluoride either by fusing and driving off hydrogen fluoride leaving the normal fluoride, or by neutralizing the acid fluoride in solution with potassium carbonate. The polyhalides of potassium were prepared by all four methods described above although method 4 was best. The salt is so unstable that at first no consistent analyses could be obtained. However, it was found that the loss of halogen occurred during separation of the crystals from the mother liquor and drying. This was obviated by collecting the crystals in a covered Jena fritted glass Gooch crucible and immediately centrifuging at high speed still keeping the potassium salt covered in the crucible. The salt was immediately transferred to tiny weighing bottles which were almost completely filled by the sample (to avoid loss of ICl_3). Excellent analyses, establishing the formula as KFICl_3 , were obtained in this fashion as shown in Table II.

Preparation of the Ammonium Fluorine Polyhalide

Pure ammonium bifluoride was almost completely neutralized with ammonia and to this cold solution a cold saturated solution of iodine trichloride was added. The yellow crystals were collected and separated from mother liquor centrifugally as in the case of the potassium salt. The analyses (Table II) showed the salt to have the formula NH_4FICl_3 .

Trihalides containing Fluorine

In addition to the fluorine pentahalides, an attempt was made to prepare the fluorine trihalides of the alkali metals by mixing a solution of the fluoride with a solution of iodine monochloride, by treating the solid fluoride with liquid iodine monochloride, and by chlorinating a suspension of iodine in an aqueous solution of the fluoride, both hot and cold. If any compound was formed it was too unstable to be isolated.

Methods of Analysis

On all the salts a complete analysis was made, save for fluorine which was determined by difference. In the first cesium fluorine polyhalide specimen prepared the cesium was determined as cesium perchlorate and in the second as cesium fluoride. It was found that the same or better results could be obtained by the latter method of gently igniting the polyhalide, whereupon all the cesium was left as cesium fluoride. This latter method was also used on the rubidium and potassium salt. In no case did the residue after ignition contain even a trace of chlorine or iodine.

The chlorine and iodine were determined by the method of Gooch. In this method two sets of samples are run, one in which the chlorine and iodine are both precipitated as the silver salts, and in the other set only the chlorine is precipitated as the silver salt. In both cases the samples were gently heated with dilute ammonium hydroxide solution to convert the chlorine and iodine into the chloride and iodide. The first set of samples were then acidified while the second were treated with dilute sulfuric acid and potassium nitrite to expel the iodine. The solution was boiled gently until the disappearance of the iodine color. The silver halides were precipitated and the chlorine determined in the usual way. If equal weight samples are used in both cases, the difference in weight in the silver salts represents the weight of silver iodide in the former case. This method is not quite as satisfactory as might be desired, due to the fact that there is danger both of not expelling all of the iodine and also of driving off some of the chlorine. The ammonium salt was analyzed for NH_3 by distilling with excess alkali, absorbing in standard acid and back-titrating; and the NH_3 was reported as NH_4F .

Properties

The cesium, rubidium, potassium, and ammonium fluorine-iodine-trichlorides have very much the same physical properties; they all have the same orange yellow color, crystalline form, and general properties but differ in their stability and the temperature at which they decompose. When the normal fluoride solution is mixed with the solution of iodine trichloride, the pentahalide separates out as brilliant, orange-yellow, needle-like, tetragonal prisms exhibiting parallel extinction under crossed nicols in two positions and isotropic in the third.

The cesium salt is the most stable. When heated in an open tube it melts and then decomposes well above 300°C .; although there is a slight decomposition below that temperature. When heated in a sealed tube it melts at 194° but on cooling there seems to have been no decomposition. The specific gravity of the CsFICl_3 is 3.565.

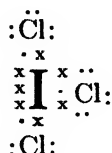
The rubidium salt is much more stable than the corresponding potassium salt but is not quite as stable as the cesium salt. When heated in an open tube the rubidium pentahalide melts and decomposes at approximately 300° . When heated in a closed tube, RbFICl_3 melts without decomposition at 172° .

The specific gravity of the rubidium polyhalide is 3.159. The potassium salt is the least stable.

When the mother liquor from which the alkali metal fluorine polyhalide is precipitated is evaporated to dryness there is very little residue left. This shows that the fluorine pentahalides are not very soluble in water. The polyhalides are not soluble in and do not react with carbon tetrachloride and are insoluble in benzene but react with it if allowed to stand in contact with it for a long period of time.

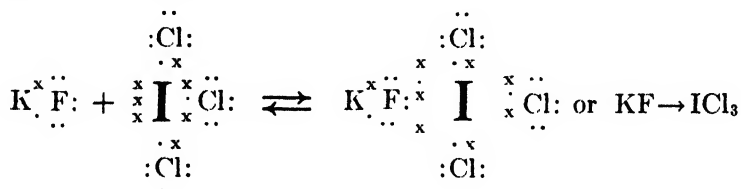
Structure

The structure of ICl_3 may be represented by



in which the central I atom has ten electrons. However, according to Sidgwick, a decet is not a particularly stable arrangement, and it is not surprising that ICl_3 tends to combine with the alkali fluorides to form pentahalides.

In this process the fluorine probably acts as a donor and the iodine as an acceptor increasing the electronic environment of the iodine to the more stable duo-decet, as follows:

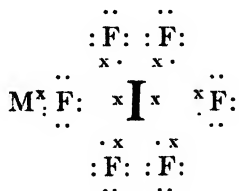


The great stability of the duo-decet is revealed in such a compound as SF_6 . As would be expected, the most stable polyhalide is formed with the alkali of highest atomic number, where the greater distance of the valence electrons from the nucleus facilitates the donation of two of the fluorine electrons.

Undoubtedly fluorine polyhalides of this same type with other metallic elements could be prepared by similar methods. Thermal analysis of the system HF-ICl_3 may also reveal new compounds.

Of this same type would be compounds formed by the union of BrF_3 with MX , yielding MFBBrF_3 , MClBrF_3 , etc.

Iodine pentafluoride should combine with alkali halides to form KXIF_5 in which two of the electrons of the iodine atom would be inert as in



Even iodine heptafluoride might combine to yield compounds of the type MXIF_8 , since the stable shell of sixteen electrons is known in such a compound as OsF_8 .

Investigation of these predicted compounds is now well under way in this laboratory, and will be reported shortly.

Summary

It was found that the most satisfactory method of preparing the fluorine polyhalides of the type formula $MFICl_3$ was to mix a saturated solution of the alkali fluoride with a saturated solution of iodine trichloride, both solutions being cold at the time of mixing.

The cesium and rubidium salts are both fairly stable, the ammonium salt less, and the potassium least, though over a long period of time the cesium and rubidium salt lose halogen unless kept in tightly stoppered bottles or in a desiccator containing a few crystals of iodine trichloride.

The fluorine polyhalides are insoluble in benzene and carbon tetrachloride but react with the former slowly. The solubility in water is limited but is greater with the ammonium and potassium salts.

The four polyhalides prepared form orange-yellow tetragonal crystals exhibiting parallel extinction.

It is established that fluorine can form part of a polyhalide.

Cleveland, Ohio.

STUDIES ON HYDRAZINE: SOLUBILITY OF HYDRAZINIUM SALTS IN MIXED SOLVENTS*

BY E. C. GILBERT AND E. H. HUFFMAN

The solubility of electrolytes in mixed solvents has been the subject of many investigations¹ but the problem is of such complexity that additional work is much to be desired. Many of the salts of hydrazine are soluble both in alcohols and in water and it was hoped that they might prove a suitable medium for an investigation over the entire field. The picrate and trinitro-*m*-cresylate were chosen particularly because their solubility, while sufficient for easy determination, is not so large as to require large amounts of material, and their solubility in water and alcohol are of the same order. They are both salts containing one equivalent of hydrazine to one of acid and are hydrated. The solubility of hydrated salts in mixtures of alcohol and water presents a special phase of the general problem and has been studied by Bödtker² and by D'Ans and Siegler.³

The solubility of picric acid in alcohol and water mixtures has also been studied.⁴ Duff and Bills found a maximum solubility in mixtures of ethyl alcohol and water containing 80% alcohol by weight. Their results differed from those of Angelescu and Dumitrescu and it was hoped that a study of the salts of the acid might show whether the increased solubility is due to the picrate ion or to the acid.

Experimental

Materials: Hydrazinium picrate and trinitro-*m*-cresylate were prepared by reaction of the base and acid in alcohol and recrystallized from water three times. This procedure leaves the picrate with one-half molecule of water and the cresylate with one molecule.

Analysis: Hydrazinium picrate; N_2H_5^+ found, 12.10, 12.12, 12.23 percent. Calc. for $\text{N}_2\text{H}_5\text{OC}_6\text{H}_2(\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, 12.23%.

Hydrazinium trinitro-*m*-cresylate; N_2H_5^+ found, 11.31, 11.25, 11.31, 11.27 percent. Calc. for $\text{N}_2\text{H}_5\text{OC}_6\text{H}(\text{NO}_3)_3\text{CH}_3 \cdot \text{H}_2\text{O}$, 11.28%.

When dried over concentrated sulfuric acid the cresylate loses its water but the picrate does not.¹ The anhydrous cresylate melts at 172-173° with decomposition.

* Contribution from the Department of Chemistry, Oregon State College.

¹ Lobry de Bruyn: *Z. physik. Chem.*, **10**, 782 (1892); Bödtker: **22**, 505 (1897); Herz and Anders: *Z. anorg. Chem.*, **52**, 164 (1907); **55**, 271 (1907); Herz and Knoch: **41**, 351 (1904); **45**, 262 (1905); Herz and Kuhn: **58**, 159 (1908); **60**, 152 (1908); Wright: *J. Chem. Soc.*, **121**, 225 (1922); Treadwell: *Helv. Chim. Acta*, **4**, 982 (1921); Angelescu and Dumitrescu: *Z. physik. Chem.*, **132**, 217 (1928); Gregg-Wilson and Wright: *J. Chem. Soc.*, **1928**, 3111; Duff and Bills: **1931**, 1196; and others.

² Bödtker: *Loc. cit.*

³ D'Ans and Siegler: *Z. physik. Chem.*, **82**, 35 (1912).

⁴ Duff and Bills: *Loc. cit.*; Angelescu and Dumitrescu: *Loc. cit.*

Commercial absolute ethyl alcohol was treated with sodium and distilled. The first and last portions were discarded. The middle portion boiling over a range of 0.02° proved to be 99.8 percent alcohol by volume and gave negative tests for aldehydes. The water was of conductivity grade.

Procedure: Mixtures of alcohol and water were made by weight and samples of the salt rotated with the solvent to constant solubility at $20^\circ \pm 0.01$. Samples were withdrawn with a pipette and the hydrazine determined by the iodic acid method.² The titration is carried out in acid solution and repeated tests showed the alcohol to be without effect on the titration.

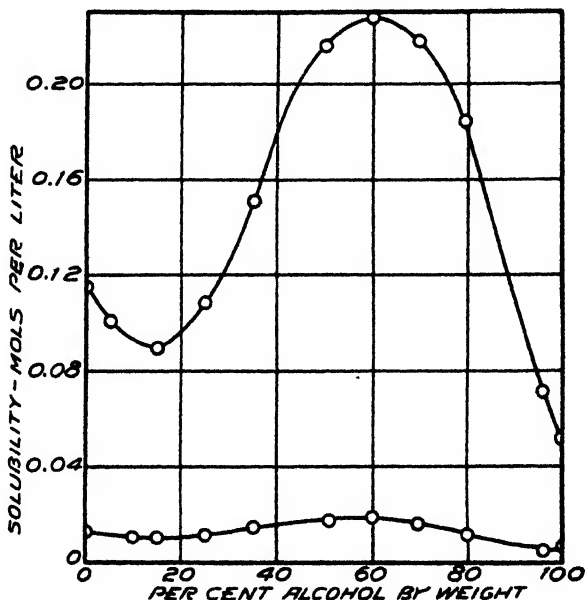


FIG. 1

Solubility of Hydrazinium Salts in Alcohol-Water Mixtures at 20° . Upper curve—Cresylate; Lower curve—Picrate

The solubility relations of the cresylate not having been previously published, the solubility curve in pure water from 15° to 30° was also determined by the same procedure.

Results and Discussion

The results are shown in Tables I and II and in Fig. 1. Both salts show very interesting solubility curves containing maxima and minima which however seem to be of doubtful value for the purpose of studying general solvent action. Due to the fact that both are plotted on the same scale the curve for the cresylate seems to have a more abrupt slope but the percentage increase or decrease in solubility is nearly the same for both salts. It is evident

¹ Gilbert: J. Am. Chem. Soc., 53, 3957 (1931).

² Bray and Cuy: J. Am. Chem. Soc., 46, 858 (1924).

TABLE I
Solubility of Hydrazinium Picrate and Trinitro-m-cresylate in Ethyl
Alcohol—Water Mixtures at 20°

Percent Alcohol by weight	Solubility	Mols/Liter
	Picrate	Cresylate
0.00	0.01396	0.1158
5.00		0.1015
10.00	0.01160	
15.00	0.01076*	0.08996
25.00	0.01113	0.1089
34.50	0.01448*	0.1509
50.00		0.2170
51.00	0.01890	
60.00	0.01901	0.2297
69.40	0.01616	0.2189
79.70	0.01176	0.1843
96.00	0.00525	0.0710
99.8**	0.00694	0.0517

* Result of one determination

** By volume

TABLE II
Solubility of Hydrazinium Trinitro-m-cresylate in Water

Temperature	Solubility Mols/Liter
15.0	0.08473
20.0	0.1158
25.0	0.1506
30.0	0.2053

that compounds, either hydrates or alcoholates, are formed in solution. These compounds are not stable in the dry state for the solid residue was removed from solutions containing 5, 60, 80, 96, and 99.8 percent alcohol, dried by washing with anhydrous ether, and in every case proved upon analysis to be the original compound. The water of hydration was retained even in 99.8 percent alcohol, but no evidence of an alcoholate was ever detected. Lobry de Bruyn¹ found certain hydrated salts which retain water even in pure alcohol, but D'Ans and Siegler² found with $\text{Ca}(\text{NO}_3)_2$ evidence of a definite alcoholate. The solubility curve in this case showed definite cusps and breaks in continuity in contrast with the smooth curves found in the present work.

The curves for the two salts show no resemblance to that of the free picric acid, perhaps due to the water of hydration, but show a general resemblance to the results of Angelescu and Dumitrescu³ for the solubility of picric acid in certain mixed organic solvents.

¹ Lobry de Bruyn: Loc. cit.

² D'Ans and Siegler: Loc. cit.

³ Angelescu and Dumitrescu: Loc. cit.

The point of maximum solubility for the salts lies in solutions of lower alcohol content than that for the free acid.¹

When solubility determinations were attempted with the anhydrous salts, they took water even from 96 percent alcohol and only when completely hydrated were concordant results obtained for the solubilities. The solubility of the picrate agrees well with earlier work² (in water). It is interesting to note that contrary to reasonable prediction, the insertion of a CH₃ group into the picrate to form the cresylate increases the solubility in water ten-fold, rather than decreasing it.

Summary

1. The solubility of hydrazinium picrate and trinitro-m-cresylate have been determined in ethyl alcohol-water mixtures at 20°.
2. Both salts give a peculiar solubility curve with maxima and minima, but no evidence was found of the formation of a stable alcoholate.
3. These salts retain their water of hydration even in 99.8% alcohol, and the anhydrous salts take up water from aqueous alcohol.
4. The solubility curve for the salts shows no resemblance to that of the free acid in the same solvents.
5. The solubility of hydrazinium trinitro-m-cresylate has been determined in water over a range of temperatures.

*Corvallis, Oregon.
July 7, 1932.*

¹ Duff and Bills: *Loc. cit.*

² Gilbert: *J. Phys. Chem.*, **33**, 1235 (1929).

DENSITIES OF SATURATED VAPOURS

BY ROBERT WRIGHT

The densities of saturated vapours have been less frequently determined than those of unsaturated. In the method here described the experimental detail is simple but the temperature of the determination is confined to that of the boiling point of the liquid yielding the vapour.

A small quantity of the liquid to be investigated is placed in a previously weighed stoppered cylindrical bulb of about 100 cc capacity. The bulb is bound by means of twine between two curved brass strips, which are soldered to two stout brass wires about 80 cm. long, care being taken that there is no direct metallic contact between the two supports. The strips should extend slightly below the bottom of the bulb, and the wires, which are soldered along the backs of the strips, should project about 1 cm beyond their lower ends. The ends of the wires below the bulb are joined by a spiral of fine platinum wire arched upwards so as to touch the bottom of the glass bulb. The upper ends of the wires pass through a cork carrying a short condenser, and the bulb and its support are suspended in the outer jacket of an ordinary Victor Meyer vapour density apparatus, in which is placed 50 — 100 cc of the liquid under investigation.

In carrying out an investigation the liquid in the jacket is boiled so that its vapour rises well above the top of the suspended bulb, which is unstoppered during the heating. The brass supporting wires are now connected to a low voltage battery and a suitable current passed through the heating spiral under the bulb. This current should be of such strength that it will evaporate the liquid in the bulb in about 15 minutes. After evaporation is complete the vapour in the bulb is at a temperature somewhat higher than its boiling point, the current is now stopped and the apparatus left for about 10 minutes till the temperature of the bulb falls to that of the surrounding boiling vapour. The bulb is now filled with saturated vapour, it is removed from the heating jacket and immediately stoppered.

After cooling to room temperature the stopper is loosened to admit air, and the bulb is weighed. Even neglecting the small volume occupied by the condensed vapour the bulb now contains less air than at its first weighing, since air is prevented from entering owing to the vapour pressure of the liquid in the bulb. The total pressure in the bulb is the barometric pressure B , and if the pressure due to the vapour is P , then the volume of air replaced by vapour = $\frac{P}{B} V$, where V is the volume of the bulb. This volume, multiplied by the weight of 1 cc of air gives the weight of air excluded from the bulb by the vapour, and this weight must be added to that obtained at the second

weighing, in order that the difference between the first and second weighings should correspond to the weight of the vapour.

The vapour pressure of the liquid at the temperature of the weighing may either be obtained from tables or else determined directly by the following simple method.

The closed end of a barometer tube is expanded into a bulb and then bent so as to lie parallel with the rest of the tube. A small quantity of the liquid under investigation is introduced into the bulb, and the open end of the tube is then fitted by means of a rubber stopper into a filter flask containing a layer of mercury. On exhausting the flask by a water pump, and slightly heating the bulb, all the air can be driven out of the barometer tube by means of the vapour stream. After disconnecting the pump, mercury rises in the tube, and allowing the apparatus to cool the vapour pressure may be read directly.

From the weight of the condensed vapour and the volume of the flask the density of the saturated vapour can be calculated. In the table are given the saturated vapour densities (grams per cc.) of a number of simple organic compounds at their boiling points, and the corresponding molecular weights calculated from the relative densities are also given. It will be seen that the molecular weights are close to the normal values except in the case of acetic acid, which is known to be associated to a considerable extent in the gaseous state. In the case of acetic acid the supporting wires were made of silver as brass is readily attacked by the vapour of the boiling acid.

The existence of a minimum in the vapour pressure curve of a binary liquid mixture is frequently assumed to indicate complex formation between the two constituents of the mixture. Such a minimum is shown by the system chloroform-

acetone, and it is of interest to determine whether the vapour of such a system shows any indication of the existence of a compound in the gaseous state.

For this purpose the saturated vapour density of the constant boiling mixture was determined, it being considered that the formation of complex molecules would be more probable in saturated than in unsaturated vapour.

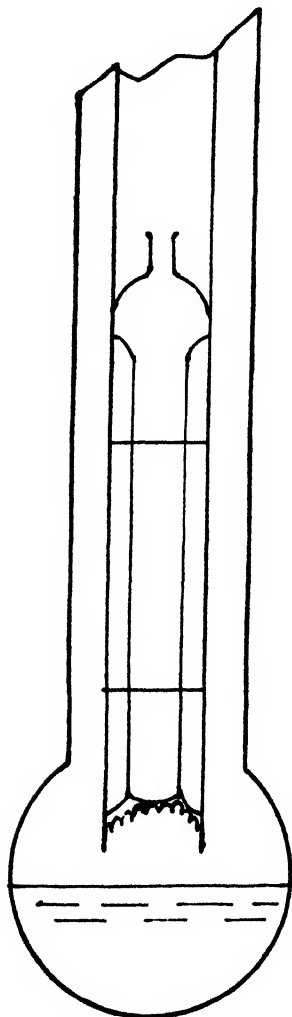


FIG. 1

The experimental values found for the vapour density relative to hydrogen in two determinations were 48 and 48.3, corresponding to molecular weights of 96 and 96.6. The refractive index of the mixture was 1.41318 corresponding to 22% acetone and 78% chloroform, or 36.5 Mol % acetone and 63.5 Mol % chloroform. On the assumption that there is no union between the molecules of the vapours, the composition corresponds to a molecular weight of 96.7, a value practically identical with the experimental figure. The results given in Table I therefore indicate that in the state of vapour there is no union between the molecules of acetone and chloroform.

TABLE I

	B. Pt.	M. Wt. (found)	M. Wt. (Cal.)	Density at 760 mm.
Alcohol	78°	46.4	46	.00162
		46.8		.00164
Benzene	80°	80.0	78	.00275
		79.6		.00274
Toluene	110°	96.0	92	.00302
		94.6		.00298
Chloroform	60°	119.0	119	.00437
		118.0		.00433
Carbon tetra-chloride	75°	158.0	154	.00452
		157.0		.00550
Acetone	56°	57.8	58	.00213
		57.4		.00211
Acetic acid	118°	100.2	60	.00314
		102.0		.00318

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THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES

IV. Arsenic Trisulfide Sol

BY HARRY B. WEISER AND GEORGE R. GRAY

In earlier papers, the displacement of chloride ions from colloidal particles by the stepwise addition of electrolytes to the positive hydrous oxide sols of iron, chromium, and aluminum, has been followed potentiometrically and the adsorption isotherms for the precipitating ions have been determined.¹ These observations have led to a proposed mechanism of the electrolyte coagulation process. The present paper deals with similar potentiometric titration and adsorption studies on negative As_2S_3 sol. This type of investigation on As_2S_3 sol should prove fruitful since Whitney and Ober,² in their classical observations on adsorption during the coagulation of this sol, pointed out that the adsorption of cations was accompanied by the setting free of an equivalent amount of acid.

Historical

Following Linder and Picton's³ observations that barium but not chlorine is carried down during the coagulation of As_2S_3 sol by BaCl_2 , Whitney and Ober investigated quantitatively the adsorption of barium, strontium, calcium, and potassium during coagulation by the respective chlorides. As a result of these studies it was concluded that equivalent amounts of the respective cations were carried down during the coagulation process. The filtrate from the coagulum contained free acid which was found by titration with alkali to be equivalent in quantity to the cation adsorbed. The phenomenon was believed by both Linder and Picton, and Whitney and Ober to be a case of hydrolytic adsorption in which equivalent amounts of cation and hydroxyl were carried down with the precipitate leaving HCl in solution. Rabinowitsch⁴ showed, however, that the adsorption does not cause hydrolytic cleavage of the salt. For example, the adsorption of barium was determined (1) from the difference in concentration of Ba^{++} ion before and after coagulation; (2) from the difference in weight of the dry As_2S_3 precipitate after coagulation with BaCl_2 and HNO_3 , respectively. The adsorption values by the two methods agreed quite well, showing that the barium was not carried down as $\text{Ba}(\text{OH})_2$. Moreover, the precipitate was free from chloride. The process would, therefore, appear to involve exchange adsorption in which hydrogen ions on the particles are exchanged for barium ions.

¹ Weiser: *J. Phys. Chem.*, **35**, 1, 1368 (1931); Weiser and Gray: **36**, 2178 (1932).

² *J. Am. Chem. Soc.*, **23**, 842 (1901).

³ *J. Chem. Soc.*, **67**, 63 (1895).

⁴ *Z. physik. Chem.*, **116**, 97 (1925).

Contrary to the belief of Whitney and Ober and of Freundlich,¹ Weiser² pointed out that the amounts of several cations carried down during the coagulation of As_2S_3 sol are not necessarily equivalent. Moreover, the amount of adsorption of a given cation varies widely with different sols, depending as it does on the method of preparation, age, and concentration of the sol.

Since the platinum and quinhydrone electrodes can not be used successfully with As_2S_3 sol, Pauli and Semler³ used conductometric methods to determine the H^+ ion concentration of a dialyzed sol and of the filtrate after coagulation of the sol by electrolytes. They found the ratio between $[\text{H}^+]$ in the filtrate and adsorbed $\frac{1}{2} [\text{Ba}^{++}]$ ion to be 4 : 1 instead of 1 : 1 as reported by Whitney and Ober. Pauli and Semler considered the sol to be a strongly dissociated complex acid to which they assigned the formula $(x\text{As}_2\text{S}_3 \cdot \text{As}_2\text{S}_4\text{H}_2 \cdot \text{As}_2\text{S}_4\text{H})' + \text{H}^+$. This formula was made to fit the specific case where but one of four H^+ ions are displaced by Ba^{++} , the remaining three appearing in solution only after coagulation.

Rabinowitsch⁴ likewise determined the H^+ ion concentration of As_2S_3 sol before and after coagulation using conductometric methods. He found the total H^+ ion concentration of the filtrate after coagulation to be equal to the $\text{Ba}^{++}/2$ adsorbed, confirming the earlier observations of Whitney and Ober. The sol was therefore assigned the general formula $[(\text{As}_2\text{S}_3)_x\text{SH}]' + \text{H}^+$, first suggested by Linder and Picton.

Since the ratios of H^+ ion in the filtrate to Ba^{++} adsorbed with different sols have been found to be 1 and 4, using similar methods of analysis, it is altogether probable that an indefinite number of different ratios could be obtained by suitable modifications in the method of preparing the sol. The formulas of Pauli and Semler and of Rabinowitsch are, therefore, without any general significance. Rabinowitsch points out that he used an undialyzed sol while Pauli and Semler used one that had been dialyzed. To the extent that dialysis influences the ratio under consideration, it is obvious that one can get considerable variation with the same preparation simply by varying the method and time of dialysis.

The conductometric method of determining the H^+ ion concentration in sol-electrolyte mixtures is of doubtful accuracy, at least in certain cases. Rabinowitsch⁵ first used a graphic method to evaluate the H^+ ion concentration from conductometric data but the results did not agree with glass-electrode measurements.⁶ Fairly good agreement was obtained if the concentration C was calculated from the expression $C = \frac{1000 X_{ac}}{u_H + u_c}$, where u_H and u_c are the mobilities of H^+ and the added cation, respectively, and

¹ Kolloid-Z., 1, 32 (1907).

² J. Phys. Chem., 29, 955 (1925).

³ Kolloid-Z., 34, 145 (1924).

⁴ Z. physik. Chem., 116, 97 (1925).

⁵ Z. physik. Chem., 116, 97 (1925); Rabinowitsch and Dorfmann: 131, 313 (1928).

⁶ Rabinowitsch and Kargan: Z. physik. Chem., 143, 21 (1929).

$$x_{ac} = x - x_0 - L \frac{\Delta x_g}{\Delta L}$$
 x and x_0 being the conductivity before and after the addition of electrolyte, L , the number of cc of electrolyte added, and $\Delta x_g/\Delta L$, the change in conductivity with change in the amount of electrolyte added after the conductivity curve assumes a straight course. For salts with univalent cations $L \frac{\Delta x_g}{\Delta L}$ has to be replaced by Δx from Kohlrausch's law, in order to get results which agree at all well with glass electrode measurements. These formulas fail to take into account both the change in activity of the added salt in the sol and the mobility of the colloidal particles. Since both of these have an effect, the method can, at best, yield only approximately accurate results. Fortunately, there is no apparent need of using a conductometric method to follow the change in hydrogen ion concentration. The glass electrode has been found satisfactory in many cases where the platinum and quinhydrone electrodes are not suitable and it would seem to be well adapted to the case at hand. Rabinowitsch and Kargan used it in three experiments to determine the change in hydrogen ion concentration during the coagulation of As_2S_3 sol, with KCl , $BaCl_2$ and $AlCl_3$, respectively; but unfortunately their data cannot be compared. The implication is that they used the same sol for all three cases but, if they did, there was something radically wrong with their procedure as the difference in pH of the original samples used with KCl and $BaCl_2$ was almost as great as the total change in pH on adding the electrolyte. In the subsequent experiments it will be shown that the glass electrode gives consistent, reproducible results with As_2S_3 sol-electrolyte mixtures.

Experimental

A. General Method of Procedure.

Preparation of Sols. The As_2S_3 sols were prepared according to the procedure of Freundlich and Nathansohn.¹ Saturated As_2O_3 solution was diluted with a solution containing 1 cc of saturated H_2S solution per 100 cc. After the appearance of a light-yellow coloration, a solution of H_2S ten times as strong as the above was added. The solution was then saturated with H_2S gas and the excess washed out with H_2 . After standing overnight, the sol was filtered and the titrations were carried out. The sol was protected at all times from the action of light. All the experiments on a given sol were completed within a few days to avoid changes brought about by ageing.

Method of Titration. To 10 cc of As_2S_3 sol contained in a weighing bottle were added varying amounts of water and precipitating electrolyte, bringing the final volume to 15 cc. A definite procedure of mixing was followed in each case. Preliminary experiments with dilute sols using 0.004 N $CaSO_4$ as coagulating electrolyte showed a decrease in pH for small amounts added, followed by an increase in pH at higher concentrations of electrolyte. This effect was found to be due to the slight alkalinity of the electrolyte (probably a trace of $Ca(OH)_2$). In all of the experiments herein recorded, the pH of the sol was first determined and then the pH of the water and of the electrolyte

¹ Kolloid-Z., 28, 258 (1921).

were brought to this value by the addition of H_2SO_4 in the case of CaSO_4 and of HCl with the several chlorides. Thus the observed displacement of H^+ ions was real, being due to the added cations and not to dilution effects. After the mixtures were made up, they were stoppered and allowed to stand in the dark for 18 hours before making the potentiometric measurements.

Potentiometric Measurements. The glass electrode was employed in the determination of H^+ ion concentration. A bulb was blown on the end of a piece of glass tubing of suitable composition.¹ The bulb was filled with 1 *N* HCl and allowed to stand in distilled water for several days before using.

In making the e.m.f. measurements a vacuum tube potentiometer constructed by Mr. M. F. Roy according to the specifications of Stadie² was employed in conjunction with a type K Leeds and Northrup potentiometer and a Hartman and Braun moving-coil galvanometer.

The glass bulb containing 1 *N* HCl was suspended in the weighing bottle containing the sol-electrolyte mixture. The tip of the salt bridge from the saturated calomel electrode making contact with the HCl , was drawn out to a fine point and plugged with cotton. To minimize the coagulation of the sol by the saturated KCl , a piece of glass tubing 3 cm long having one end covered with cellophane and containing distilled water, was attached to the tip of the bridge arm making contact with the liquid in the weighing bottle. This tube was removed and flushed out after each measurement.

To calculate the pH from the e.m.f. measurements the glass electrode was standardized with *M*/20 potassium acid phthalate, which has a pH of 3.97.³ The solution was placed in a weighing bottle and all contacts were made in the manner outlined above. The pH of the sol-electrolyte mixture is given by the formula: $\text{pH of mixture} = 3.97 \pm \frac{\text{e.m.f. of phthalate} - \text{e.m.f. of mixture}}{0.0001984T}$

In subsequent tables the e.m.f. of the potassium acid phthalate solution is designated " E_0 ". This method of standardization eliminates errors due to inequalities between the calomel electrodes and to liquid-liquid contact potentials. Other standard buffers of lower pH were frequently run as controls.

B. Variation in Hydrogen Displacement with Concentration of Sol.

Sols of different concentrations were investigated to find a satisfactory one for simultaneous measurements of hydrogen displacement and cation adsorption. It would be expected that with sols prepared under similar conditions, the most concentrated sol would show the greatest hydrogen ion displacement. This view was confirmed by the following experiment: As_2S_3 sols I, II, and III, containing 1.70, 4.38, and 10.80 g/l, respectively, were titrated with 0.004 *N* CaSO_4 . Most of the data are recorded in Table I, but to conserve space a portion of the observations are omitted after the pH value attained a constant value. All of the H^+ ion displacement data are shown graphically in Fig. 1.

¹ McInnes and Dole: *J. Am. Chem. Soc.*, **52**, 29 (1930). Glass used was from Corning Glass Co., their No. 015.

² *J. Biol. Chem.*, **83**, 477 (1929).

³ Clark and Lubs: *J. Biol. Chem.*, **25**, 506 (1916); Clark: "The Determination of Hydrogen Ions," 3rd. ed. 485 (1928).

TABLE I
Titration of As_2S_3 Sols with 0.004 N CaSO_4
(10 cc of sol. Total volume 15 cc. 30°C)

Cc of 0.004 N CaSO_4 added	π milli- volts	pH	$[\text{H}] \times 10^5$ in solution	$[\text{H}] \times 10^5$ displaced	$\frac{1}{2} [\text{Ca}] \times 10^5$ added
Sol I 1.70 g/l $E_0 = 169.6$ mv					
0.0	170.2	3.98	10.5	0.0	0.0
0.5	164.1	3.88	13.2	2.7	13.3
1.0	164.3	3.88	13.2	2.7	26.7
1.5	163.6	3.87	13.5	3.0	40.0
2.0	164.9	3.89	12.9	2.4	53.3
2.5	163.9	3.88	13.2	2.7	66.7
3.0	164.1	3.88	13.2	2.7	80.0
5.0	164.2	3.88	13.2	2.7	133.3
Sol II 4.38 g/l $E_0 = 182.5$ mv					
0.0	154.9	3.51	30.9	0.0	0.0
0.5	151.5	3.45	35.5	4.6	13.3
1.0	149.5	3.42	38.0	7.1	26.7
1.5	150.1	3.43	37.2	6.3	40.0
2.0	149.7	3.42	38.0	7.1	53.3
2.5	148.9	3.41	38.9	8.0	66.7
3.0	149.2	3.42	38.0	7.1	80.0
5.0	149.0	3.41	38.9	8.0	133.3
Sol III 10.80 g/l $E_0 = 165.4$ mv					
0.0	125.4	3.30	50.1	0.0	0.0
0.5	119.7	3.21	61.7	11.6	13.3
1.0	118.1	3.18	66.1	16.0	26.7
1.5	116.9	3.16	69.2	19.1	40.0
2.0	116.2	3.15	70.8	20.7	53.3
2.5	115.9	3.14	72.5	22.4	66.7
3.0	115.4	3.14	72.5	22.4	80.0
5.0	115.5	3.14	72.5	22.4	133.3

The displacement follows a smooth course similar to the usual adsorption isotherm. It is of interest to note that the maximum displacement of hydrogen ions occurs before the precipitation concentration (approximate value indicated by a vertical line cutting the curve) is reached. A similar behavior was reported with BaCl_2 by Rabinowitsch and Fodimann,¹ who confirmed Briggs²

¹ Z. physik. Chem., 154 A, 255 (1931).

² J. Phys. Chem., 34, 1326 (1930).

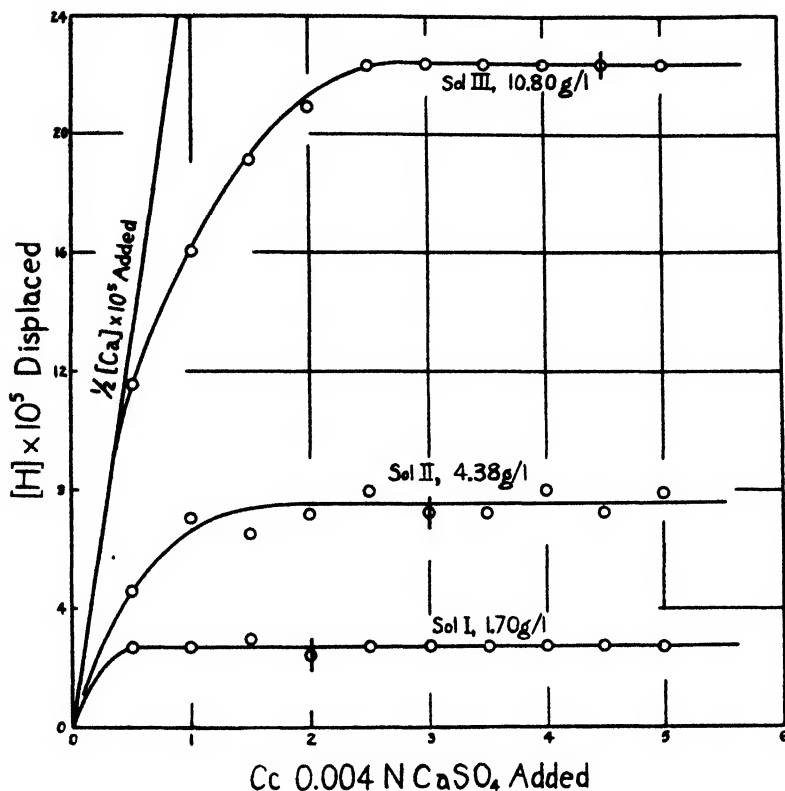


FIG. 1

Hydrogen Ion Displacement Curves for As_2S_3 Sols of Different Concentrations

observation that the cataphoretic migration velocity attains a minimum value well below the precipitation concentration of BaCl_2 but not of AlCl_3 . Except with low concentrations of electrolyte and concentrated sols, the amount of hydrogen displaced is distinctly less than the amount of calcium added.

The total displaced hydrogen is 20%, 21% and 31% of the total hydrogen in the filtrate after coagulation of sols I, II and III, respectively.

C. Displacement of Hydrogen Ions and Adsorption of Cations

I. Observations on As_2S_3 Sol IV

Titration Experiments. The above experiments having indicated that a sol containing 10 g/l would show a satisfactory displacement of hydrogen ions, a sol of approximately this composition (10.64 g As_2S_3 per l) was prepared and titrated with the chlorides of barium, strontium, calcium, aluminum, and ammonium, employing the method previously described. Most of the titration data for the salts with multivalent cations are given in Table II and all of the data are shown graphically in Fig. 2.

TABLE II

Titration of As_2S_3 Sol IV with 0.004 N Solutions of BaCl_2 , SrCl_2 , CaCl_2 and AlCl_3 (10 cc. of sol. Total volume 15 cc. 30°C)

Solution added cc	π milli-volts	pH	$[\text{H}] \times 10^4$ in solution	$[\text{H}] \times 10^4$ displaced	Equivalents of electrolyte $\times 10^4$, added
I. BaCl_2 $E_0 = 157.4$ mv					
0.0	120.8	3.36	43.7	0.0	0.0
0.5	115.5	3.28	52.5	8.8	13.3
1.0	113.0	3.24	57.5	13.8	26.7
1.5	110.7	3.20	63.1	19.4	40.0
2.0	108.3	3.16	69.2	25.5	53.3
2.5	107.9	3.15	70.8	27.1	66.7
3.0	107.5	3.14	72.5	28.8	80.0
5.0	106.3	3.13	74.1	30.4	133.3
II. SrCl_2 $E_0 = 154.5$ mv					
0.0	118.0	3.36	43.7	0.0	0.0
0.5	113.1	3.28	52.5	8.8	13.3
1.0	110.7	3.24	57.5	13.8	26.7
1.5	107.5	3.19	64.6	20.9	40.0
2.0	105.8	3.16	69.2	25.5	53.3
2.5	105.1	3.15	70.8	27.1	66.7
3.0	104.8	3.14	72.5	28.8	80.0
5.0	103.8	3.13	74.1	30.4	133.3
III. CaCl_2 $E_0 = 148.6$ mv					
0.0	112.6	3.37	42.7	0.0	0.0
0.5	108.0	3.29	51.3	8.6	13.3
1.0	105.2	3.25	56.2	13.5	26.7
1.5	102.3	3.20	63.1	20.4	40.0
2.0	100.5	3.17	67.6	24.9	53.3
2.5	100.0	3.16	69.2	26.5	66.7
3.0	99.5	3.15	70.8	28.1	80.0
5.0	98.4	3.14	72.5	29.8	133.3
IV. AlCl_3 $E_0 = 162.0$ mv					
0.0	125.1	3.36	43.7	0.0	0.0
0.5	119.0	3.25	56.2	12.5	13.3
1.0	115.9	3.20	63.1	19.4	26.7
1.5	113.9	3.17	67.6	23.9	40.0
2.0	113.2	3.16	69.2	25.5	53.3
2.5	112.8	3.15	70.8	27.1	66.7
3.0	113.4	3.16	69.2	25.5	80.0
3.5	113.1	3.15	70.8	27.1	93.3
4.0	112.3	3.14	72.5	28.8	106.7
4.5	111.6	3.13	74.1	30.4	120.0
5.0	111.3	3.13	74.1	30.4	133.3

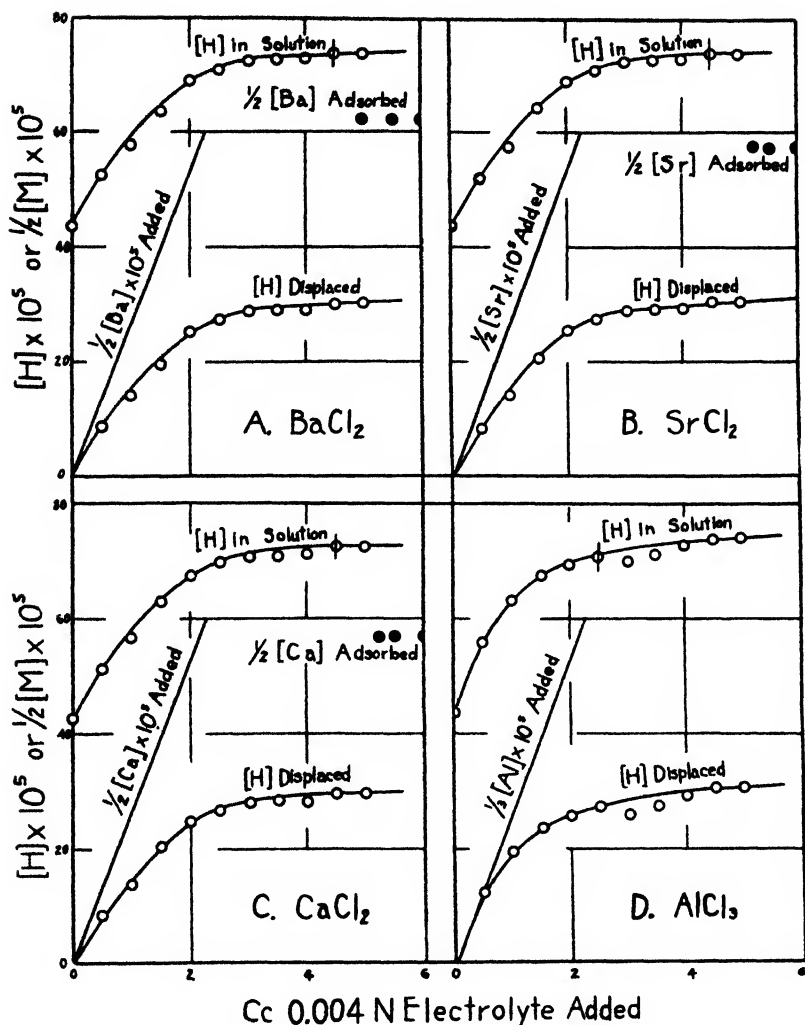


FIG. 2

Titration Curves of As_2S_3 Sol IV. A with BaCl_2 , B with SrCl_2 , C with CaCl_2 , and D with AlCl_3 .

Since 5 cc of 0.004 N NH_4Cl did not bring about the coagulation of 10 cc of sol, the experiments were continued with 0.01 N, 0.04 N, and 0.5 N solutions. Coagulation occurred on the addition of 1.5 cc of 0.5 N solution. The abridged data are given in Table III and Fig. 3. For the same concentration of 0.004 N solution the displacement is only one-half as great as with electrolytes having multivalent cations. The increase in the amount displaced after the first 2 cc is quite gradual.

TABLE III

Titration of As_2S_3 Sol IV with NH_4Cl
(10 cc. of sol. Total volume 15 cc. 30°C)

Cc of NH_4Cl added	π Milli- volts	pH	$[\text{H}] \times 10^5$ in solution	$[\text{H}] \times 10^5$ displaced	$[\text{NH}_4] \times 10^5$ added
Series I. $E_0 = 150.5 \text{ mv}$					
0.0	114.6	3.37	42.7	0.0	0.0
0.004 N 0.5	114.2	3.36	43.7	1.0	13.3
1.0	112.0	3.33	46.8	4.1	26.7
1.5	110.1	3.30	50.1	7.4	40.0
2.5	108.5	3.27	53.7	11.0	66.7
3.0	108.2	3.36	54.9	12.2	80.0
5.0	106.1	3.23	58.9	16.2	133.3
Series II. $E_0 = 157.4 \text{ mv}$					
0.0	120.7	3.36	43.7	0.0	0.0
0.01 N 2.0	113.2	3.23	58.9	15.2	133.3
3.0	111.6	3.21	61.7	18.0	200.0
0.04 N 2.0	109.1	3.17	67.6	23.9	533.3
0.5 N 1.5	108.7	3.16	69.2	25.5	5000.0
5.0	108.1	3.15	70.8	27.1	16666.7

The discussion of these results will be delayed until the adsorption results are given.

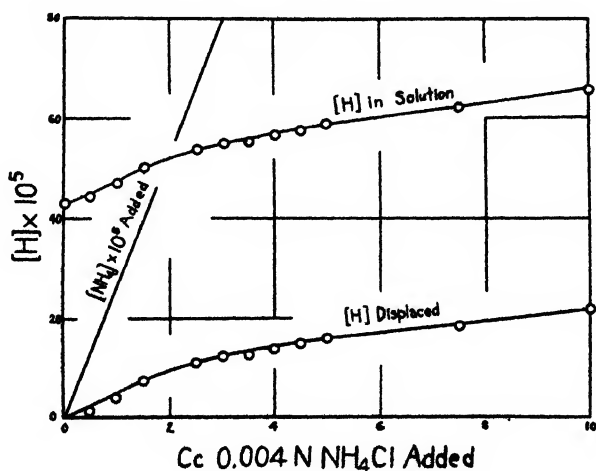


FIG. 3
Titration Curves of As_2S_3 Sol IV with NH_4Cl

Adsorption Experiments. The measurement of the adsorption of cations above the coagulation point was carried out as follows: To 100 cc of sol contained in a wide-mouth bottle, varying amounts of water and 0.01 *N* electrolyte were added, the final volume being 150 cc. After standing stoppered in the dark for 18 hours, the precipitate was matted down by centrifuging and the supernatant liquid filtered through a small filter paper to remove traces of As_2S_3 . A 100 cc portion was taken for analysis. The barium and strontium were determined as sulfates and the calcium was precipitated as oxalate and weighed as oxide. For standardization, a sample in which water was substituted for the sol was subjected to the same treatment. The results are given in Table IV and shown on the respective titration curves in Fig. 2. The amounts adsorbed are not quite equivalent, the Ba^{++} ion being

TABLE IV

Adsorption of Ba, Sr, and Ca during the Coagulation of As_2S_3 Sol IV
(100 cc of sol. Total Volume 150 cc)

Cc 0.01 <i>N</i> solution added	mg adsorbed	milli- equivalents per g As_2S_3	Equivalents $\times 10^4$ adsorbed	Equivalents $\times 10^4$ added
BaCl_2	BaSO_4	Ba	Ba	Ba
20.0	11.3	0.091	64.5	133.3
22.0	11.3	0.091	64.5	146.7
24.0	11.3	0.091	64.5	160.0
SrCl_2	SrSO_4	Sr	Sr	Sr
21.0	8.0	0.082	58.0	140.0
22.0	7.9	0.081	57.3	146.7
24.0	7.9	0.081	57.3	160.0
CaCl_2	CaO	Ca	Ca	Ca
21.0	2.4	0.081	57.1	140.0
22.0	2.4	0.081	57.1	146.7
24.0	2.4	0.081	57.1	160.0

taken up in slightly greater amount¹ than the Sr^{++} and Ca^{++} . The sol was exhausted before the observations with Al could be made. Later results with another sol show that the adsorption of Al is about the same as that of Ba at a concentration 47% lower than the Ba concentration.

Discussion of Results. A comparison of the H^+ ion displacement curves with multivalent ions, Fig. 2, reveals a marked similarity in form. The curves with Ba and Sr are almost identical while the displacement with Ca is distinctly less and with Al greater at low concentrations, than that of Ba. With the divalent ions the displacement curve flattens out before complete coagulation takes place, and the cataphoretic velocity reaches a constant minimum value below the precipitation value of the electrolyte.² This may be con-

¹ Cf. Weiser: *J. Phys. Chem.*, **29**, 955 (1925).

² Briggs: *J. Phys. Chem.*, **34**, 1326 (1930).

nected with the relatively slow course of the coagulation in the immediate region of the precipitation value. If sufficient time were allowed, coagulation would probably take place at electrolyte concentrations which give a constant minimum cataphoretic velocity and a constant maximum displacement of H^+ ion. With $AlCl_3$, which precipitates in appreciably lower concentration than the chlorides of the divalent metals, the maximum displacement of hydrogen ion occurs slightly above the precipitation value while the cataphoretic velocity is still on the decrease.¹

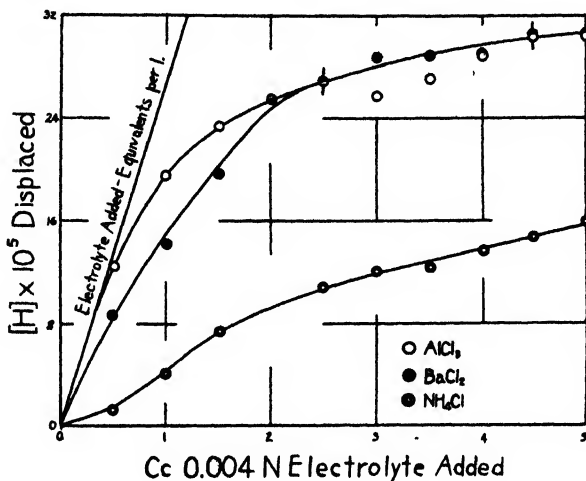


FIG. 4
Hydrogen Ion Displacement Curves of As_2S_3 Sol IV
with Cations of Varying Valence

The displacement curves for cations of varying valence are shown in Fig. 4. The marked displacing action of the Al, especially at low concentrations, is in line with the higher precipitating power of $AlCl_3$, while the relatively weak displacing action of NH_4 is in accord with the relatively low precipitating action of NH_4Cl . An analogous behavior was observed with positive sols.²

The curves in Fig. 2 show that in the sol under investigation, somewhat more than one-third of the total H in solution after coagulation was displaced from the particles, the remainder being measurable potentiometrically in the original sol. In all cases a portion of the H was derived from H_2S in the intermicellar solution; but even if the solution were saturated with H_2S , this would account for only about 10% of the H^+ ion concentration.

The adsorption of the several cations was approximately twice as great as the hydrogen displaced. This means that a portion of the adsorbed cation corresponds to H measurable potentiometrically in the original sol. The adsorption was from 14% to 22% less than the total H in solution after coagulation instead of being equal to the H^+ ion concentration, as found by Whitney and Ober.

¹ Loc. cit.

² Weiser: J. Phys. Chem., 35, 1, 1368 (1931).

II. Observations on As_2S_3 Sol V

As a check on the observations recorded in the previous section, some experiments were carried out with a sol containing 20 g As_2S_3 per liter.

Titration Experiments. Titrations were made exactly as previously described with the chlorides of Al, Ba and NH_4 . A portion of the results are given in Table IV and all of them, except for high concentrations of NH_4Cl , are shown graphically in Fig. 5.

TABLE IV

Titration of As_2S_3 Sol V with $AlCl_3$, $BaCl_2$ and NH_4Cl
(10 cc of sol. Total volume 15 cc. 30°C)

	Cc of solution added	π milli- volts	pH	$[H] \times 10^4$ in solution	$[H] \times 10^4$ displaced	Equivalent of electrolyte $\times 10^4$ added
I. $AlCl_3$ $E_o = 148.0$ mv						
	0.0	94.1	3.07	8.5	0.0	0.0
0.004 N	0.5	90.1	3.01	9.8	1.3	1.3
	1.0	87.4	2.96	11.0	2.5	2.7
	1.5	85.9	2.94	11.5	3.0	4.0
	2.0	85.3	2.92	12.0	3.5	5.3
	2.5	84.4	2.91	12.3	3.8	6.7
	3.0	83.5	2.90	12.6	4.1	8.0
	4.5	82.4	2.88	13.2	4.7	12.0
	5.0	82.7	2.88	13.2	4.7	13.3
II. $BaCl_2$ $E_o = 147.4$ mv						
	0.0	93.4	3.07	8.5	0.0	0.0
0.004 N	0.5	90.8	3.03	9.3	0.8	1.3
	1.0	87.9	2.98	10.5	2.0	2.7
	1.5	87.3	2.97	10.7	2.2	4.0
	2.0	87.1	2.96	11.0	2.5	5.3
	2.5	85.5	2.94	11.5	3.0	6.7
	3.0	84.2	2.92	12.0	3.5	8.0
	4.0	82.9	2.90	12.6	4.1	10.7
	5.0	82.2	2.88	13.2	4.7	13.3
0.01 N	3.0	81.4	2.87	13.5	5.0	20.0
	3.5	81.5	2.87	13.5	5.0	23.3
III. NH_4Cl $E_o = 148.3$ mv						
	0.0	94.5	3.07	8.5	0.0	0.0
0.004 N	1.0	92.3	3.04	9.1	0.6	2.7
	2.0	90.8	3.01	9.8	1.3	5.3
	3.0	89.2	2.99	10.2	1.7	8.0
	5.0	88.3	2.96	11.0	2.5	13.3
0.04 N	1.0	85.9	2.93	11.7	3.2	26.7
	3.0	84.1	2.90	12.6	4.1	80.0
0.5 N	0.75	83.6	2.89	12.9	4.4	250.0
	3.0	83.4	2.88	13.2	4.7	1000.0

Adsorption Experiments. The adsorption of Al and Ba was determined by the procedure previously described except that in the case of Al, 250 cc of sol were used and the final volume was 375 cc. A 325 cc sample was taken for analysis and after evaporation to 50 cc, the Al was precipitated with NH_4OH and weighed as Al_2O_3 . It seemed impractical to attempt to determine the adsorption of NH_4^+ ion from change in concentration since the percentage

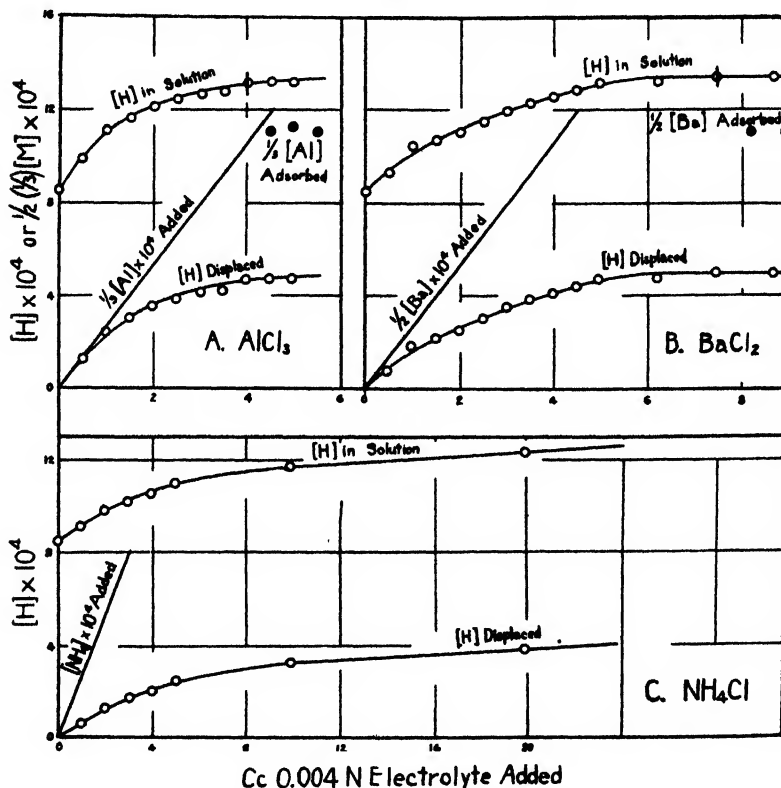


FIG. 5

Titration Curves of As_2S_3 Sol V. A with AlCl_3 , B with BaCl_2 , and C with NH_4Cl

change is so slight compared with the amount required for coagulation. The adsorption data are given in Table V and in Fig. 5.

Discussion of Results. As would be expected, the titration and adsorption data on the stronger sol V exhibit relationships which are quite similar to those with the more dilute sol IV. The H^+ ion concentration of the stronger sol is approximately twice that of the weaker but the total hydrogen ions displaced during the coagulation of the stronger sol is only approximately 1.7 times as great as with the weaker sol. This means that relatively more of the H^+ ions are measurable potentiometrically in the stronger sol than in the weaker. Of the total H^+ ion concentration in the supernatant liquid after coagulation with

TABLE V

Adsorption of Al and Ba during the Coagulation of As_2S_3 Sol V

Cc 0.01 N solution added	mg adsorbed	milli- equivalents per g As_2S_3	Equivalents $\times 10^4$ adsorbed	Equivalents $\times 10^4$ added
(With $AlCl_3$ 250 cc sol. Total volume 375 cc)				
$AlCl_3$	Al_2O_3	Al	Al	Al
45.0	7.1	0.083	11.1	12.0
50.0	7.2	0.085	11.3	13.3
55.0	7.0	0.082	11.0	14.7
(With $BaCl_2$ 100 cc of sol. Total volume 150 cc)				
$BaCl_2$	$BaSO_4$	Ba	Ba	Ba
33.0	19.4	0.083	11.1	22.0
35.0	19.4	0.083	11.1	23.3
36.0	18.7	0.080	10.9	24.0

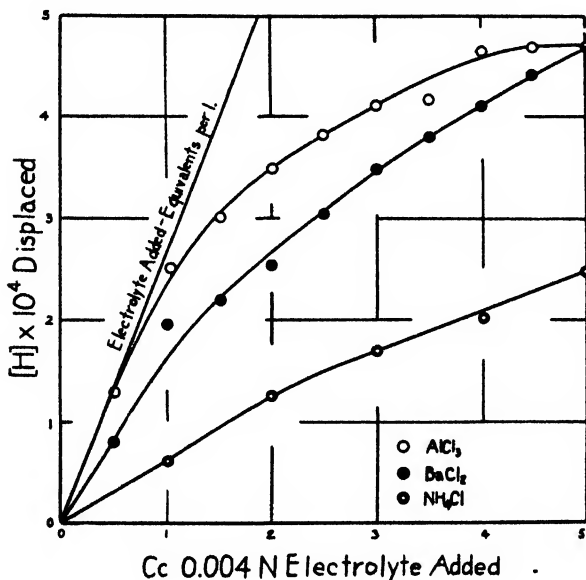


FIG. 6

Hydrogen Ion Displacement Curves of As_2S_3 Sol V
with Cations of Varying Valence

divalent ions, approximately 36% was displaced from the colloidal particles as compared with 20% from sol I, 21% from sol II, 31% from sol III and 41% from sol IV. Obviously the amount of displaceable H on the colloidal particle is not determined exclusively by the concentration of the sol but depends on the particle size and the conditions of formation.

The displacement curves for the three types of salts are shown together in Fig. 6. Again it will be noted that at lower concentrations aluminum has a greater displacing power than Ba, and NH_4 , a much weaker displacing power than the multivalent ions.

The adsorption of Al and Ba in equivalents is of the same order of magnitude in the region of the precipitation value for the respective salts, but the precipitation value of the Ba is 87% greater than that of Al. From the slope of the H⁺ ion displacement curves it appears that the adsorption of Ba is distinctly less than the adsorption of Al at a concentration of BaCl₂ corresponding to the precipitation value of AlCl₃. Indeed, the adsorption of aluminum is practically complete up to, and including, the precipitation concentration of AlCl₃, whereas only one-half the precipitation concentration of Ba is adsorbed.

Constitution of Arsenic Trisulfide Sol and the Mechanism of the Coagulation Process

Since precipitated As₂S₃ is quite hydrous, the composition of the body of the particles may be represented by the general formula $x\text{As}_2\text{S}_3 \cdot y\text{H}_2\text{O}$, the value of x and y being determined by the condition of formation and the age of the sol. The particles are negatively charged and since the chief electrolyte in the intermicellar solution is H₂S, it is probable that the inner portion of the double layer surrounding the particles is chiefly the HS⁺ ion derived from the primary dissociation of this acid. The anions of arsenious acid or of a thioacid may constitute a portion of this inner layer. The outer portion of the double layer is a diffuse layer of H⁺ ions, many of which have sufficient osmotic pressure that they influence the H electrode and can be measured potentiometrically. The constitution of a colloidal particle is represented diagrammatically in Fig. 7. The hydrogen ions within the dotted circle are so firmly held by the attraction of the adsorbed HS⁺ layer that they do not influence the H electrode. Others with a higher kinetic energy, shown beyond the dotted circle, are measurable potentiometrically with the glass electrode. A small portion of the H⁺ ions are derived from the dissociation of H₂S in the intermicellar solution.

On adding an electrolyte such as BaCl₂ to the sol the strongly adsorbed Ba⁺⁺ ions enter the outer layer, displace H⁺ ions, and take up a position relatively closer to the inner layer than the H⁺ ions, as shown diagrammatically in Fig. 8. This decrease in thickness of the double layer and increase in charge density of the outer layer, result in a lowering of the charge on the particles to the point where collisions result in partial coalescence and agglomeration. Because of the stronger adsorption of the Al⁺⁺⁺ ions the thickness of the double layer is less than with divalent Ba. Accordingly, less Al needs to be adsorbed to reduce the charge to the coagulation point and precipitation takes place with lower concentrations of Al salts than of Ba salts. With the weakly adsorbed ions such as NH₄⁺, a relatively high concentration is necessary to increase the charge density in the outer layer and so lower the charge to the coagulation point. Because of the weaker adsorption of NH₄⁺ than of Al and Ba, the displacement of H by NH₄ from the portion of the outer layer represented within the dotted circle is much less than with an equivalent amount of the multivalent ions.

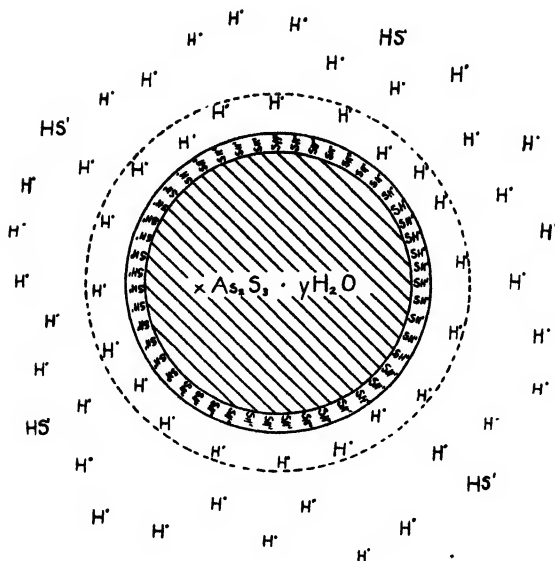


FIG. 7

Diagrammatic Representation of the Structure of the Micelle in the original As_2S_3 Sol

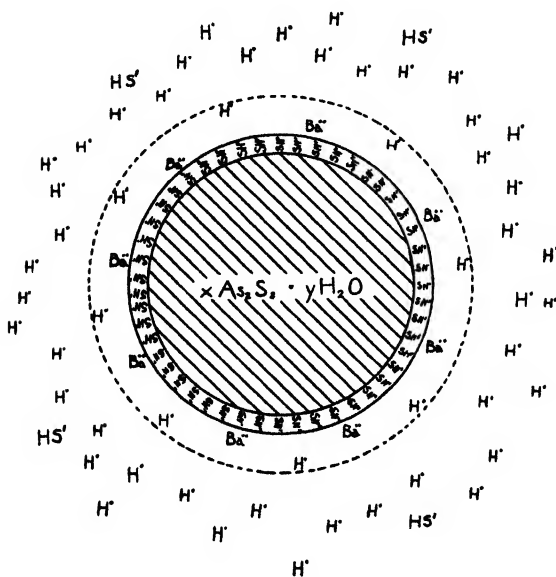


FIG. 8

Diagrammatic Representation of the Structure of the Micelle in As_2S_3 Sol after adding some $BaCl_2$

The adsorption of multivalent cations at their precipitation value is much greater than the hydrogen displaced. The reason is obvious since a part of the adsorbed ion takes the place of hydrogen in the outer portion of the double layer and so increases the charge density of the outer layer. The adsorption is in general less than the total concentration in the filtrate after coagulation. It was a fortuitous combination of circumstances that gave Whitney and Ober a filtrate having the same amount of H^+ ions as the amount of metallic ions adsorbed.

Summary

The following is a brief summary of the results of this investigation.

1. Supplementing the classical observations of Whitney and Ober on adsorption during the coagulation of As_2S_3 sol, the glass electrode has been employed in a study of the changes in H^+ ion concentration during the stepwise addition of precipitating electrolytes to the sol.

2. The H^+ ion displacement curve follows a smooth course, similar in form to an adsorption curve. The displacement is relatively greater at lower concentrations and attains a maximum at or below the so-called precipitation value of the electrolytes.

3. In the sols investigated the total amount of displaced H^+ ion varies from 20% to 40% of the total H^+ ion concentration of the supernatant liquid after coagulation of the sol. The amount of displaced H^+ is not determined exclusively by the concentration of the sol but depends on the conditions of formation of the sol as they influence the size and form of the particles.

4. In all cases, the adsorption of precipitating ions is appreciably less than the total H^+ ion concentration of the filtrate after coagulation. The two values will be equal only under a fortuitous combination of conditions.

5. The amount of displaced H^+ is less than the amount of precipitating ion adsorbed. A part of the adsorption corresponds to H^+ in the diffuse outer layer of the particles, which is measurable potentiometrically in the original sol.

6. The order of displacing power of the several chlorides is: $Al > Ba, Sr > Ca > NH_4$. This is likewise the order of the precipitating power of the several electrolytes and the order of adsorption of the several cations at concentrations below the precipitation value.

7. A diagrammatic representation of the constitution of the colloidal particles is given to account for the above results; and an adsorption mechanism of the neutralization process leading up to coagulation, is outlined.

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GLYCINE IN WATER SOLUTION*

BY JESSIE Y. CANN

A study of the structure of glycine from the absorption spectra of the compound dissolved in water, in hydrochloric acid solution and in sodium hydroxide solution has just been made by Anslow, Foster and Klingler.¹ They also made a study of the freezing points of glycine in water solution. Using their experimental data for freezing points, we, in this paper, have calculated various thermodynamic functions, and have considered glycine as a micelle.

The term micelle, meaning an aggregation of ions or molecules in solution, acting as a unit, has been used by several authors.² Hoskins, Randall and Schmidt have studied the activity coefficients of glutamic and aspartic acids. Although these are di-carboxylic acids, the authors assumed that the ionization of the second carboxyl was negligible. Glycine, or amino-acetic acid, has been compared with these acids, considered as micelles, and striking resemblances occur.

Table I contains all the calculated thermodynamic data. The first two columns give the molalities, m , and the freezing point depressions, θ , obtained by Anslow, Foster and Klingler.¹ In column eleven are given the activity coefficients, calculated according to the equations for concentrated solutions given by Lewis and Randall.³ In the fifth column are given the values of

of $j = 1 - \frac{\theta}{\nu \lambda m}$, where θ = the depression of the freezing point, ν the number of ions assumed at infinite dilution, λ the molecular depression of water i.e. 1.858° , and m the molality. The value for ν was taken as 2, on the assumption that glycine is a uniunivalent electrolyte.

Log j was next plotted against log m , and the values of α and β determined.³ The value for α was taken as 0.3 and that for β as 0.534. Then j was plotted against log m , and the values of the function $\int_0^m j d \log m$ obtained from the areas under the curve, to each of which was added the area from infinite dilution up to molality = 0.01, obtained from the equation,

$$\int_0^{0.01} j d \log m = - \frac{\beta}{2.303\alpha} (0.01)^\alpha$$

* Contribution from the Chemical Laboratory of Smith College.

¹ Anslow, Foster and Klingler: Unpublished work.

² a. McBain and Salmon: *J. Am. Chem. Soc.*, **42**, 426 (1920); b. Randall, McBain and White: **48**, 2517 (1926); c. Randall and Cann: **50**, 347 (1928); d. Randall and Cann: *Chem. Reviews*, **7**, 369 (1930); e. Hoskins, Randall and Schmidt: *J. Biol. Chem.*, **88**, 215 (1930).

³ Lewis and Randall: "Thermodynamics," pp. 342, 346, 347 (1923).

TABLE I

$\alpha = 0.3$			$\beta = 0.534$			
m	θ	log m	m [†]	$j = 1 - \frac{\theta}{\nu \lambda m}$	$\frac{j}{m^{\dagger}}$	log j
0.010	0.029	2.0000	0.1000	0.2196	2.1959	1.3416
0.100	0.195	1.0000	0.3162	0.4752	1.5029	1.6769
0.210	0.389	1.3222	0.4583	0.5015	1.0944	1.7003
0.385	0.710	1.5855	0.6205	0.5037	0.8118	1.7022
0.572	1.035	1.7574	0.7563	0.5131	0.6784	1.7102
0.765	1.382	1.8837	0.8746	0.5139	0.5875	1.7108
0.986	1.769	1.9939	0.9930	0.5171	0.5207	1.7136
1.200	2.121	0.0792	1.0955	0.5244	0.4787	1.7196
1.500	2.679	0.1761	1.2248	0.5194	0.4241	1.7155

m	θ	$\int_0^m j \, d \log m$	$\frac{j}{2.303}$	$-\log \gamma$	γ	K
0.010	0.029	0.1942	0.0954	0.2896	0.5129	5.40×10^{-3}
0.100	0.195	0.5631	0.2064	0.7695	0.1700	3.48×10^{-3}
0.210	0.389	0.7203	0.2178	0.9381	0.1151	3.14×10^{-3}
0.385	0.710	0.8515	0.2187	1.0702	0.0851	3.05×10^{-3}
0.572	1.035	0.9402	0.2228	1.1630	0.0687	2.90×10^{-3}
0.765	1.382	1.0039	0.2231	1.2270	0.0593	2.86×10^{-3}
0.986	1.769	1.0551	0.2245	1.2796	0.0525	2.87×10^{-3}
1.200	2.121	1.1002	0.2277	1.3279	0.0470	2.78×10^{-3}
1.500	2.679	1.1517	0.2255	1.3772	0.0420	2.76×10^{-3}

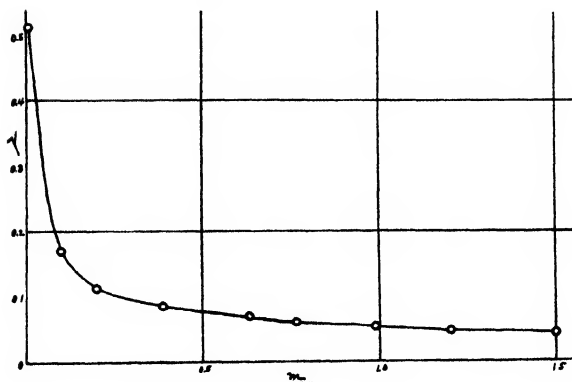
The values for the total areas are given in column ten. Then the activity coefficients, γ , were calculated from the equation,

$$\log \gamma = \int_0^m j \, d \log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} \, d \theta$$

The last term was neglected. The values of the activity coefficients are listed in the thirteenth column.

It will be noticed that the values of γ are small, as was to be expected. This is in agreement with the values obtained by Hoskins, Randall and Schmidt²⁶ for glutamic and aspartic acids. We therefore assume that glycine associates or forms micelles in concentrated solutions. This is also in agreement with the results of Anslow, Foster and Klingler¹ in postulating polymerization in concentrated solutions.

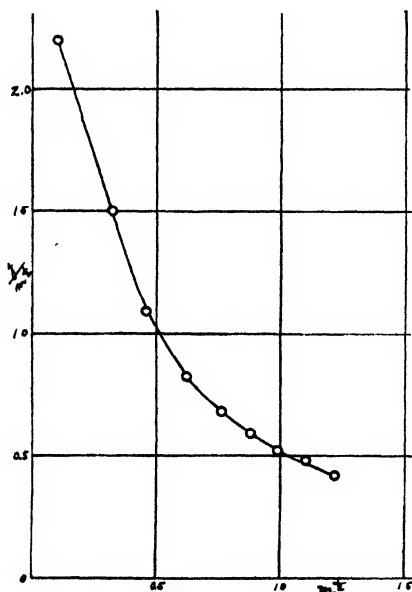
In Curve I we have plotted the values of γ against m. In Curve II we have plotted the values of j/m^{\dagger} against m^{\dagger} . This curve shows that the results



CURVE I

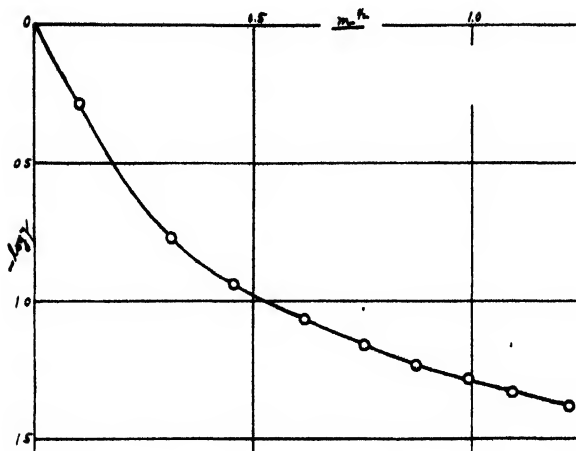
are in agreement with those obtained for other substances by the authors² who have assumed micellation. In Curve III we have plotted $-\log \gamma$ against $m^{\frac{1}{2}}$ and find that it can be compared favorably with the composite curve of Randall.⁴

For curiosity, we have calculated values of K on the basis that glycine dissociates in water solution into two ions. We have therefore taken K to be equal to $(m \gamma)^2 / m(1 - \gamma)$. These values are listed in column fourteen of



CURVE II

⁴ Randall: J. Chem. Educ., 8, 1066 (Fig. 2) (1931).



CURVE III

Table I. The values of K_a and K_b , as determined by Branch and Mijamoto,⁵ are really hydrolysis constants. They are also considered as such by Adams⁶ and by Bjerrum.⁷

The conclusion of this study is that glycine, considered as a micelle in concentrated solutions, shows good agreement with other substances considered thermodynamically on the same basis.

⁵ Branch and Mijamoto: J. Am. Chem. Soc., **52**, 863 (1930).

⁶ Adams: J. Am. Chem. Soc., **38**, 1503 (1916).

⁷ Bjerrum: Z. physik. Chem., **104**, 147 (1923).

SILICON HYDRIDE, MONATOMIC, OR TRIATOMIC HYDROGEN

BY A. B. VAN CLEAVE* AND A. C. GRUBB†

In a note,¹ G. R. Schultz criticises a paper² by one of the authors and his co-workers. Objection was made to the assumption that the active hydrogen studied in this investigation was triatomic. Our critic considers that this activity can be explained in a more plausible manner on the basis of monatomic hydrogen. In the same note and a subsequent paragraph, the statement is made that from the results of his own work no definite assertion can be made about the existence of either monatomic or triatomic hydrogen.

In using either explanation, an assumption would have to be made. Experimental evidence seems to indicate that very little monatomic hydrogen exists above 1 mm. pressure. Kaplan³ found that at 1 mm. pressure, he could not obtain atomic hydrogen in any quantity through a 1.5 cm. glass tube into a bulb. B. Lewis⁴ explains the discrepancy between his results and those of Koenig and Elöd⁵ on the basis of recombination of atoms. The former employed pressures of 0.04 to 0.1 mm. and the latter workers 10 mm. to 15 mm. Lewis considered that at 15 mm. pressure hydrogen atoms would recombine before reaching the mixing point.

Other investigators have drawn conclusions about the existence of triatomic hydrogen after attempting to repeat and confirm the experimental results of some of the exponents of this theory. In one particular investigation,⁶ from the description of the procedure used it is known that confirmation was not possible.

Very rapid advances are being made in theoretical physics and chemistry. But often these advances are the necessary outgrowth of inadequate explanations offered for some experimental fact by the existing theory. Already the latest theories have been found to be inadequate in some cases as pointed out by several investigators.⁷ The theory of Heitler and London⁸ which was applied to normal atoms in S states may be nearly correct, but for atoms in other states the theory falls short of general application. If atoms are in an excited state Kemble and Zener⁹ found that the nuclear symmetry characteristic is a most important factor influencing their interaction. For atoms in P states some investigators find that orbital angular momentum considerations are of importance. The evidence for the existence of a triatomic hydrogen ion, H_3^+ , has been confirmed by a number of investigators. However, H. S. N. Massey,¹⁰ after an extensive mathematical treatment of the triatomic hydrogen ion, H_3^+ , by methods used by Heitler and London, states:

"The equilibrium separation cannot be fixed with any certainty and it is still doubtful whether we must regard H_3^+ ion as a true homopolar compound

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or a polarization compound. It would appear that the electron pair is not quite strong enough to hold the extra proton."

It seems from this investigation that the existence of the triatomic hydrogen ion, H_3^+ , may also be doubtful on the same principles that deny existence to the neutral triatomic molecule. The latest investigator¹¹ who tries to prove that triatomic hydrogen does not exist would explain all reactions on the basis of silicon hydride. The perfect blank runs repeatedly confirmed during the investigation by Binder, Filby, and Grubb do not support the theory that silicon hydride produced the results that were found. Since the publication of Hiedemann's paper, our former results have been confirmed and extended. A special investigation of blank runs was made. From the discharge the hydrogen was pumped through an ammonia free and very dilute sulphuric acid solution for an hour. Upon adding Nessler's reagent no ammonia like precipitate was formed. Similar runs were made by passing hydrogen from the discharge in contact with a paper dipping into a solution of lead acetate. No sign of a brown color appeared after an hour exposure to the stream of hydrogen. These blank runs were tried repeatedly and in no case did we find any indication of activity that might be attributed to silicon hydride. But during a regular run with the gas passing in contact with plastic sulphur a paper becomes heavily coated with lead sulphide in less than ten minutes. We find no evidence to support the silicon hydride explanation for hydrogen activity and consider it a factor not applicable under our experimental conditions.

During the investigation of the properties of atomic hydrogen, R. W. Wood¹² found that a fragment of tungsten, platinum or thoria became incandescent in a stream of atoms. This test has been used by other workers when studying the properties of hydrogen atoms. We tried this test a large number of times under our experimental conditions and found no detectable heating effect upon the exposed metallic fragment.

On the basis of the amount of sulphide produced in ten minutes during a regular run one would expect considerable heating effect on a metallic fragment if the activity were due to atoms. We have found no evidence to indicate that the activity of hydrogen studied by Binder, Filby and Grubb was due to hydrogen atoms or silicon hydride. Consequently we consider that we are justified in maintaining the original assumption that the activity found is due to triatomic hydrogen.

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THE FARADAY—EFFECT OF SOME UNI-UNIVALENT ELECTROLYTES IN AQUEOUS SOLUTIONS. I

BY E. BUCH ANDERSEN AND R. W. ASMUSSEN

The magnetic rotation of the plane of polarisation is, in analogy with refractive index, specific heat, etc., to a certain extent an additive property so that an atom, which enters a molecule, approximately always gives the same contribution to the molecule's magnetic rotation, independently of the remaining components of the molecule, but often dependent on the kind of link which is formed. As will be known from Perkin's investigations on organic substances, the rotation is sometimes suitable for the settling of problems of constitution.

Whilst the experimental material with respect to organic substances may be considered tolerably complete, this in no way applies to the inorganic compounds. The inorganic substances, whose magnetic rotation has been measured, give the impression of having been chosen by chance or investigated from some special physical point of view.¹ A systematic experimental material on inorganic compounds does not exist.

From the measurements already published it can be seen that the rotation of salts in solutions is approximately determined additively as the sum of the ions' rotation. A mixture of two salts in solution can give a rotation, which is the sum of those of the components. But the constitution has an effect here also, since, if complex salts are formed, the result will be quite different. It would, therefore, seem possible also within the bounds of inorganic chemistry to use this property for the settling of questions of constitution in the chemistry of complex salts.

But, furthermore, the measurement of the magnetic rotation gives information (so far in very implicit form), which can be expected to be valuable for the theoretical understanding of molecular structure. The magnetic rotation of the plane of polarisation is a dispersion phenomenon, a kind of Zeeman effect. And just as the investigation of the Zeeman effect on a spectral line from an atom in a gas gives information about the nature of the stationary states of the atom, between which the transition takes place, so the Faraday-effect in connection with knowledge of the substance's absorption spectrum and dispersion may be an important aid in the study of molecular stationary states.

We have tried in this work to procure some systematical material for a series of simple substances. The investigation covers different compounds of the cations H, Li, Na, Rb, Cs and NH₄ with the anions F, Cl, Br, I, OH, ClO₃, BrO₃ and IO₃. These ions are all diamagnetic in their normal state (more complicated relations supervene with paramagnetic substances, Ladenburg²) and,

¹ Only the work of Jahn (*Ann. Physik*, **43**, 280 (1891)) is of a more surveying character as far as the inorganic material of his paper is considered. Jahn measured a few salts of Li, Na, K, Sr, Cd and Mn, the results being in good general agreement with the corresponding measurements of ours.

² *Z. Physik*, **46**, 168 (1927).

since all measurements are made with light from the visible spectrum, they have been carried out in a part of the spectrum far from any absorption bands. We have not had any precision apparatus at our disposal. Our figures are, therefore, to be considered as a survey material and, in consequence of the whole position, intended more for drawing comparisons between these ions mutually than for a profound investigation of the properties of the individual ion.

The rotation of the investigated solutions has been measured for light of wave length $546\mu\mu$ and with water as standard substance. We have followed the common practice and given as results the "Verdet-constant" (V) of the solutions and the "molecular rotation" (M) of the dissolved substances. M is given with water's molecular rotation under the same conditions as unity. The absolute values for V have been calculated from Verdet's constant for water, which according to Rodger and Watson¹ for Na-light is:

$$V_{\text{water}} = 0.01311 - 0.064t - 0.074t^2.$$

V is here expressed in minutes of arc and t is a temperature between 4° and 98° . As is to be expected V is for diamagnetic substances only in a slight degree dependent on the temperature. According to our measurements with water at 0°C , $V_{546\mu\mu} = 1.183 \cdot V_{589\mu\mu}$.

In order to calculate the molecular rotation of a dissolved substance from the measured rotation of the solution it is assumed that the dissolved substance and the solvent act independently of each other, and that the measured rotation is composed additively from the rotation of these two. This assumption leads to the following expression for the molecular rotation of the dissolved substance (with water's molecular rotation equal to 1), when the dissolving medium is water:

$$M = \frac{D_2}{D_1} \cdot \frac{(\mu m_1 + m_2)}{dm_1} - \mu$$

where

M is the molecular rotation of the dissolved substances ($M_{\text{water}} = 1$),

D_1 is the measured angle of rotation for water

D_2 is the measured angle of rotation for the solution

m_1 is the molecular weight of water,

m_2 is the molecular weight of the dissolved substance,

μ is the number of gram molecules of water per gram molecule of dissolved substance,

d is the density of the solution (water = 1) at the temperature at which the rotation angle is measured.

It is to be expected that the assumption mentioned above will not hold in every case and it also turns out that the molecular rotations vary with the concentration of the solutions, sometimes even rather greatly.

¹ Z. physik. Chem., 19, 357 (1896).

Experimental Technique

The apparatus which we used was built up of units procured from a Laurent polarimeter. The polarizing Nicol was fixed in such a way that it could be easily moved and replaced so as to permit the tube to be placed inside the solenoid. When the Nicols were set for complete extinction one half of the field of view transmitted a slight amount of light. The reason for this was that the Laurent polariscope originally had been constructed for the use of sodium light, whereas we used the green mercury line. It was, however, very easy to decide when the two halves of the field of view were of equal colour-intensity.

The polarisation tube was 40 cm long (volume ca. 35 cm³). It was in nearly the whole of its length (ca. 38 cm) surrounded by a solenoid of copper wire (diameter of wire 1.5 mm). The total copper weight amounted to ca. 20 kg, and the resistance of the solenoid at room temperature was ca. 7 ohm. To obtain fairly large rotation angles for measurement, currents of 20-23 amps. were used, which correspond to effects of 3000-3700 watts. This naturally caused a rapid heating of the solenoid.

In view of the rotations-dependence upon temperature special precautions must be adopted to preserve the solutions at a constant and well-defined temperature during the measurements. The polarisation tube was, for this purpose, surrounded by a jacket with water and chopped ice, since we found, that, under the given conditions, this was the simplest and most effective method of preventing a rise in temperature in the solutions under investigation. All our measurements are therefore taken at 0°C. To prevent condensation of water vapour a stream of dry air was sometimes during the measurements blown over that end of the polarisation tube, which turned towards the observer.

As a source of light a quartz mercury lamp was used and the desired line was isolated from the mercury spectrum by means of a Wratten filter No. 77a (special green Hg-line) and a liquid filter consisting of a solution of 18 g didymium chloride in 50 cm³ of water in a thickness of 1 cm.

The solutions under investigation were produced from the purest possible materials (eventually after thorough purifying of these) and their concentration determined by analysis (at least two determinations for each solution). The density at 0° was measured by weighing out in a calibrated pycnometer (ca. 15 cm³).

The optical measurements were made in the following manner. The polarisation tube with the solution was set aside to cool with ice for ca. 1 hour, while care was taken that an abundant quantity of ice was continually present. Thereafter, together with an abundant supply of ice, it was placed in the polarisation apparatus. The current (and with it the strength of the magnetic field) altered its value somewhat rapidly during the measurements, and it was found to be difficult to keep the current constant by means of a variable resistance. We therefore decided to let one observer undertake the adjustment of the optical apparatus, while the other at a given signal read the current in the solenoid on a precision amperemeter. Each solution was measured four

times all together (twice by each observer); similarly the zero position of the apparatus was determined twice by each observer before and after every such set of measurements. The rotation angles were first corrected for the rotation of the empty tube ($6'$), then reduced to the same current, and finally the four single determinations were brought to an average, which is given as result in the table.

The measured rotation angles lay between 18° and 70° . The polarisation apparatus was provided with nonius which allowed the angle to be read with an accuracy of $1'$. The alteration of the field strength caused, however, a considerably larger error. For the sake of control, we have repeated the measurements with a number of solutions, and have every time been able to reproduce the results with some few per mille deviations. The error in the measured angles will in general scarcely exceed $\frac{1}{2}\%$ of the value. An examination of the significance of the remaining sources of error shows that the uncertainty of the final M-values should not exceed 2% .

Results

All our measurements are, as mentioned, carried out at 0°C . Since the rotation of water has been used as unity, we have measured the effect for this substance several times, evenly distributed over the whole period, Table I. We have therewith aimed partly at getting a good determination of this constant and partly at controlling the working conditions.

TABLE I

Water's rotation at 0°C . $\lambda = 546\mu\mu$

20.76°	20.72°
20.68°	20.71°
20.69°	20.76°
20.63°	20.74°
20.76°	20.57°

$$20.70^\circ \pm 0.020^\circ$$

All these rotation angles are reduced to an arbitrarily chosen but fixed current ($i = 100$ scale divisions on the amperemeter, corresponding to ca. 19 amps.). The current was as a rule greater during the measurements. From the measurements with water it can be calculated that the reduced rotation angles correspond to a magnetic potential difference of ca. 80,000 Gauss. cm between the ends of the tube or an average field strength of ca. 2,000 Gauss along the tube.

Table II gives the results of our measurements. The letters used have the same meaning as mentioned before. V is the Verdet-constant in minutes of arc. The column " $\%$ " gives the solution's percentage contents of the stated substance. The angles are reduced to the same current as for water.

TABLE II
Magnetic Rotation of the Polarisation Plane. °C. $\lambda = 546\mu$

Substance	m	%	μ	d	D_2/D_1	V	M
KF	58.10	45.96	3.791	1.3815	1.0304	0.0160	1.44
KF	—	21.46	11.80	1.2034	1.0242	0.0159	0.99
HCl	36.47	16.22	10.46	1.0826	1.2976	0.0201	4.51
HCl	—	7.612	24.57	1.0402	1.1386	0.0177	4.55
LiCl	42.40	29.31	5.675	1.2403	1.5425	0.0239	4.31
LiCl	—	13.05	15.69	1.0785	1.2198	0.0189	4.72
NaCl	58.46	25.41	9.526	1.2040	1.3845	0.0215	5.16
NaCl	—	12.80	22.10	1.0992	1.1845	0.0184	5.22
KCl	74.56	21.24	15.35	1.1480	1.2227	0.0190	5.41
KCl	—	15.34	22.84	1.1059	1.1643	0.0181	5.57
RbCl	120.96	30.17	15.54	1.2833	1.2469	0.0193	6.09
RbCl	—	21.77	24.13	1.1846	1.1527	0.0179	5.89
CsCl	168.26	59.62	6.325	1.7425	1.5324	0.0238	7.45
CsCl	—	36.27	16.41	1.3779	1.2541	0.0195	7.03
CsCl	—	14.06	57.01	1.1206	1.0816	0.0168	6.51
NH ₄ Cl	53.50	19.54	12.25	1.0596	1.2918	0.0200	6.31
NH ₄ Cl	—	12.54	20.71	1.0407	1.1807	0.0183	5.79
HBr	80.93	43.41	5.855	1.4327	2.0053	0.0311	8.63
HBr	—	20.60	17.31	1.1629	1.3952	0.0216	8.85
LiBr	86.86	45.27	5.828	1.4663	2.0043	0.0311	8.73
LiBr	—	23.70	15.52	1.2029	1.4435	0.0224	8.89
NaBr	102.92	40.06	8.543	1.4278	1.7773	0.0276	9.21
NaBr	—	25.58	16.62	1.2407	1.4309	0.0222	9.14
KBr	119.02	33.32	13.23	1.3033	1.4961	0.0232	9.54
KBr	—	24.30	20.58	1.2058	1.3304	0.0206	9.42
RbBr	165.42	45.92	10.81	1.4907	1.5599	0.0242	10.11
RbBr	—	30.94	20.48	1.2882	1.3415	0.0208	10.41
NH ₄ Br	97.96	26.79	14.86	1.1749	1.4546	0.0226	10.27
NH ₄ Br	—	20.05	21.68	1.1244	1.3285	0.0206	10.37
LiI*	133.86	23.04	24.82	1.2009	1.6092	0.0220	18.40
NaI	149.92	60.98	5.325	1.8532	3.3585	0.0521	19.41
NaI	—	34.88	15.53	1.3624	1.9601	0.0305	18.95
KI	166.02	51.51	8.674	1.5799	2.4855	0.0386	19.48
KI	—	39.75	13.96	1.3987	1.9797	0.0307	19.85
NH ₄ I	144.96	55.10	6.555	1.5166	2.8145	0.0437	20.55
NH ₄ I	—	35.13	14.86	1.2793	1.9488	0.0302	20.04
NaOH	40.01	12.98	14.88	1.1613	1.1754	0.0182	2.43
KOH	56.11	14.78	17.96	1.1474	1.1275	0.0175	2.75
NH ₄ OH	35.05	10.25	17.03	0.9790	1.0333	0.0160	3.00
NaClO ₃	106.46	43.26	7.757	1.3771	1.1188	0.0174	3.35
NaClO ₃	—	23.91	18.80	1.1941	1.0580	0.0164	3.10
NaBrO ₃	150.92	19.86	33.78	1.1918	1.1304	0.0175	6.21
LiIO ₃	181.86	28.03	25.90	1.3034	1.3077	0.0203	10.22

* As it was impossible to obtain a colourless solution of LiI this substance has been measured with yellow light ($\lambda = 578 \mu\mu$, $D_1 = 18.027^\circ \pm 0.015^\circ$).

The solutions of sodium and potassium hydroxide were prepared from Merck's reagents in tablets, which should have a specially small content of carbonate. The solutions were analysed immediately after the optical measurements and the stated results give the total amount of alkali calculated as hydroxide. Special investigations showed that the carbonate content in the two solutions was less than 2% of the amount of hydroxide. We have not made any correction for this, since the carbonate-ion and the hydroxyl-ion have almost the same rotation.

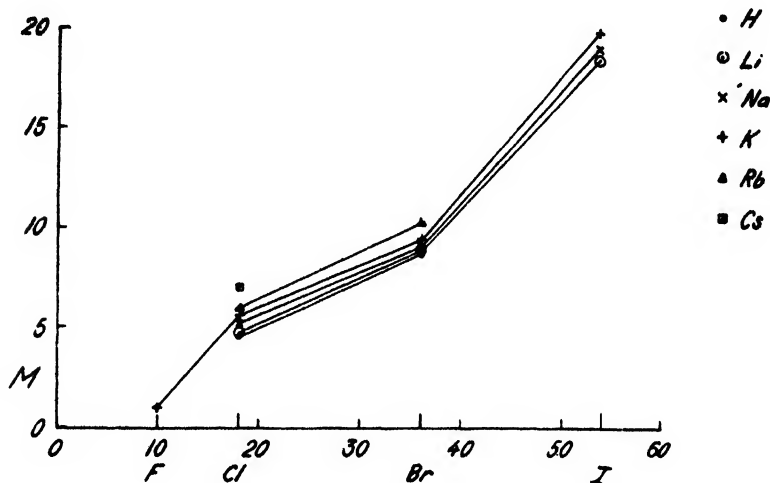


FIG. 1

The LiIO_3 -solution gave after preparation a slight sediment (probably a basic salt). For this reason we determined the content of both Li and IO_3 in the solution. The Li-content was found to be a little too low in proportion to the amount of iodate (2% of the value). The concentration given in the table refers itself to the amount of iodate, and in the calculation of M we have also followed this, since the rotation of the Li-ion compared with that of the IO_3 -ion is very slight.

All substances, investigated in solutions of different concentration, show that M varies with the concentration (in many cases, however, within the error of measurement). The variation is specially large for KF .

In Fig. 1 the results are plotted graphically. Ordinates are the compound's molecular magnetic rotation for green light in solutions with μ equal to 15-25, abscissa the anion's atomic number. It is evident from the figure that the rotation of these compounds can approximately be composed additively by the rotation of the two ions. Further it may be seen that a change of the anion with the same cation gives a large change in the rotation, while change of the cation with the same anion gives only a slight variation in M .

The molecular magnetic rotation of the individual ions can only be computed if the value for one of them is arbitrarily fixed. We can regard the rotation of the hydrogen ion equal to 0. (This would be strictly true if the

hydrogen ion in solutions was identical with a hydrogen nucleus). On this assumption the following "ionic rotations" may be computed from our measurements.

TABLE III

Cation	M	Anion	M
H	0.00	F	0.39
Li	0.11	Cl	4.43
Na	0.13	Br	8.97
K	0.60	I	10.04
Rb	1.45	OH	2.15
Cs	2.08	ClO ₃	1.76
NH ₄	1.00	BrO ₃	4.77
		IO ₃	10.12

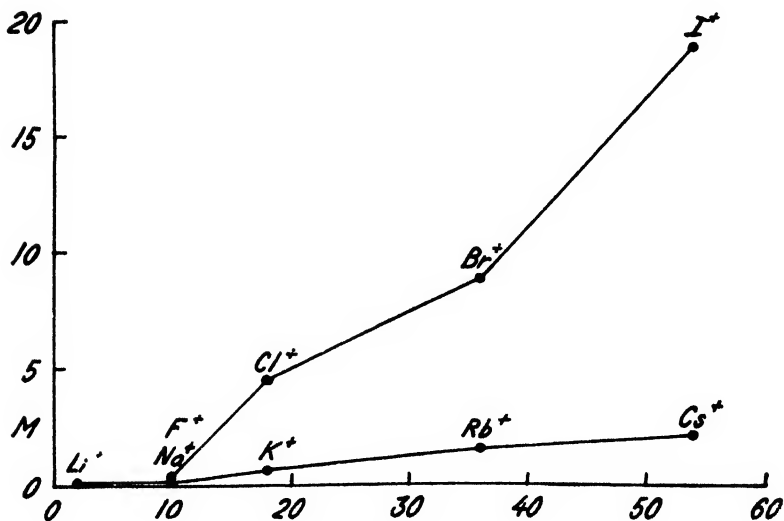


FIG. 2

This table is shown graphically in Fig. 2. The curves correspond completely in form and position to the analogous curves for ionic volumina and refraction. The additive relations are, however, only approximately valid. A test shows that deviations of systematic character appear between the observed values for M and those calculated by means of the table. It must be expected that exact additive relations of this kind only exist for very dilute solutions.

Our figures give some good examples of how the rotation of an individual atom depends upon the kind of chemical linkage. In Table IV is stated how much the molecular rotation of halogen compounds is increased when an atom of chlorine is substituted with bromine or an atom of bromine with iodine. The figures for halides and oxyacids are taken from our own measurements, the figures for organic compounds from earlier determinations of Perkin and others.

TABLE IV

	MX	MXO ₃	Org. Comp.
Br — Cl	4.53	3.01	1.83
J — Br	10.07	5.35	4.20

We shall not here attempt to discuss these relations any closer. In conclusion we shall only call attention to a few remarkable facts which have been made evident by the investigation, namely that the rotation of water is nearly one half of the sum of that of hydrogen ion and hydroxyl ion, while a solution of ammonia in water has a rotation equal to the sum of rotations for ammoniumion and hydroxyl ion.

We thank the director of the laboratory, Prof. Dr. Julius Petersen, for his kind permission to use the means of the laboratory for this work.

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THE FARADAY-EFFECT OF ELECTROLYTES IN AQUEOUS SOLUTIONS. II

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In the previous work¹ we published measurements of the Faraday-effect for 43 aqueous solutions of simple inorganic compounds. We could demonstrate that the so-called relative molecular rotation of these compounds can approximately be computed by adding together the rotations of the ions in question, which later we determined from the material as a whole, taking the rotation of the hydrogen ion as equal to 0. Our material was comprised of compounds of the cations H, Li, Na, K, Rb, Cs and NH₄ with the anions F, Cl, Br, I, OH, ClO₃, BrO₃ and IO₃.

In the present work we have continued our efforts to bring forth a more systematical inorganic material, having measured the rotation of a further 42 aqueous solutions comprising a number of compounds of alkali-ions with especially sulphurous anions. Besides these, some other compounds have been introduced. The material has been so chosen that it should give information as to how the magnetic rotation of certain compounds will be altered when an oxygen or sulphur atom is added, or when an oxygen atom is replaced by a sulphur atom. In this way is produced a new collection of examples showing the extraordinary importance of the constitution with regard to the magnetic rotation.

Our apparatus is the same as was used in the last work and the earlier treatise contains a detailed description of the experimental technique. All measurements have again been taken at 0°C and for the wavelength 546μ. A small alteration in our method of working has been introduced, as we no longer determine the zero position of the polarisation apparatus with each individual measurement. By turning the current in the solenoid the rotation is measured alternately on both sides of the zero-point, the position of this being thus eliminated.

Table I contains the results of our measurements. The first column gives the substance measured. We have, just as in the previous case, used the purest possible substances for preparation of the solutions, which substances have in several cases been subjected to further purification. We prepared some compounds ourselves.

The second column (m) gives the molecular weight of the material measured. The third column (%) gives the percentage of the substance contained in the solutions. The figures have been determined by analysis. Further details about some of the methods of analysis are given below. μ is the amount of g-mol. of water per g-mol. of dissolved substance in the solution. It may be seen from the table that we, in the present work, have been measuring

¹ J. Phys. Chem., **36**, 2819 (1932).

TABLE I

Magnetical Rotation of the Polarisation Plane. °C. $\lambda = 546\mu\mu$

Substance	m	%	μ	d	D_2/D_1	V	M
H ₂ O ₂	34.016	30.42	4.319	1.1229	0.9792	0.0152	1.09
H ₂ O ₂	—	15.67	10.16	1.0620	0.9930	0.0154	1.10
H ₂ O ₂	—	10.52	16.06	1.0413	0.9947	0.0154	1.08
H ₂ S	34.086	0.2303	819.7	1.0000	1.0043	0.0156	5.37
K ₂ S	110.27	19.23	25.71	1.2084	1.4570	0.0226	12.67
K ₂ S	—	3.681	160.16	1.0410	1.0811	0.0168	12.52
KCN	65.108	35.39	6.595	1.1869	1.1597	0.0180	3.38
KCN	—	18.66	15.75	1.0973	1.0945	0.0170	3.57
KCN	—	2.883	121.7	1.0184	1.0159	0.0158	3.31
KOCN	81.108	3.905	110.8	1.0259	1.0069	0.0156	2.37
KSCN	97.178	63.65	3.081	1.3925	1.8401	0.0285	8.12
KSCN	—	25.99	15.36	1.1441	1.2934	0.0201	8.10
KSCN	—	4.140	124.9	1.0222	1.0453	0.0162	8.33
NH ₄ SCN	76.118	21.32	15.59	1.0541	1.2998	0.0202	8.84
NH ₄ SCN	—	3.276	124.8	1.0076	1.0437	0.0162	8.84
CO(NH ₂) ₂	60.048	5.513	57.13	1.0177	1.0152	0.0158	3.18
CO(NH ₂) ₂	—	2.415	134.7	1.0075	1.0077	0.0156	3.35
CS(NH ₂) ₂	76.118	6.071	65.37	1.0206	1.0979	0.0170	9.17
CS(NH ₂) ₂	—	3.093	132.4	1.0105	1.0516	0.0163	9.79
SOCl ₂	118.99	100	0	1.6754	2.1827	0.0339	4.66
SO ₂ Cl ₂	134.99	100	0	1.7087	1.3485	0.0209	1.53
H ₂ SO ₄	98.09	3.870	135.2	1.0287	1.0030	0.0156	1.93
(NH ₄) ₂ SO ₄	132.15	38.25	11.84	1.2321	1.0737	0.0167	4.87
(NH ₄) ₂ SO ₄	—	5.146	135.2	1.0355	1.0185	0.0158	4.99
(NH ₄) ₂ S ₂ O ₈	228.22	30.89	28.34	1.1897	1.0204	0.0158	6.83
(NH ₄) ₂ S ₂ O ₈	—	7.867	148.4	1.0445	1.0029	0.0156	6.26
Na ₂ SO ₃	126.07	8.565	74.71	1.0998	1.0977	0.0170	7.24
Na ₂ SO ₃	—	3.475	194.4	1.0528	1.0506	0.0163	6.58
Na ₂ S ₂ O ₃	158.14	29.87	20.61	1.2825	1.3106	0.0203	9.42
Na ₂ S ₂ O ₃	—	6.033	136.7	1.0525	1.0565	0.0164	9.33
K ₂ S ₂ O ₃	190.34	40.64	15.43	1.3687	1.3368	0.0207	9.96
K ₂ S ₂ O ₃	—	7.341	133.4	1.0586	1.0505	0.0163	9.47
(NH ₄) ₂ S ₂ O ₃	148.22	56.59	6.311	1.3152	1.5863	0.0246	11.22
(NH ₄) ₂ S ₂ O ₃	—	5.875	131.8	1.0350	1.0516	0.0163	10.47
Na ₂ S ₂ O ₆	206.14	8.622	121.3	1.0675	1.0239	0.0159	6.00
K ₂ S ₂ O ₆	270.41	8.859	154.4	1.0607	1.0280	0.0159	9.79
K ₂ S ₂ O ₆	—	8.263	166.6	1.0565	1.0263	0.0159	9.82
K ₂ S ₄ O ₆	302.48	13.60	106.7	1.0932	1.0618	0.0165	13.24
K ₂ S ₄ O ₆	—	12.70	115.4	1.0858	1.0591	0.0164	13.56
K ₂ S ₅ O ₆	334.55	6.737	248.1	1.0832	1.0669	—	16.87
K ₂ CO ₃	138.20	47.79	8.381	1.5114	1.1164	0.0173	3.48
KHCO ₃	100.11	17.22	26.71	1.1214	1.0214	0.0158	2.68

* The potassium pentathionate solution contains further potassium chloride; refer to text.

solutions decidedly more diluted than in the previous experiments, since both the empiric agreement between the individual measurements and calculation of the probable error have proved the justification of this extension of the field of measurement. We have not yet, however, been able to work with "diluted solutions" as these are understood in physical chemistry.

d is the specific gravity of the solution at 0° in relation to water at 0° . D_2/D_1 indicates the rotation of the solution at 0° relative to that of water at the same temperature and in the same thickness of layer, reduced to the same current in the solenoid. The rotation of water was measured regularly throughout the whole work; Altogether 88 determinations of this quantity have been made. The rotation of each solution was measured from 4 to 8 times (2 to 4 times by each observer), this being divided as a rule on two working days. The figures in the table represent the average of these measurements. The measured (double) angles of rotation were of the order of magnitude 30° - 40° . V is Verdet's constant in minutes of arc, calculated as described in our earlier paper. Finally, M is the relative molecular rotation of the dissolved substance, when the molecular rotation of water is fixed equal to 1. The error in the quoted values of M will be ca. 1%.

As to the methods of preparation and analysis we shall give some brief particulars.

H_2S was determined by oxidation with iodine and titration by Volhard's method.

K_2S was prepared by ourselves. The sulphide was determined by oxidation with hypobromite and iodometric titration after the method of Willard and Cake.²

$KOCN$ prepared by ourselves, recrystallized from methyl alcohol. Analysis according to Mellor.³

$SOCl_2$ and SO_2Cl_2 . Kahlbaum's preparates. Purified by redistillation.

Na_2SO_3 . Analysis by Willard and Cake's method.²

$Na_2S_2O_6$. Kahlbaum's preparate, twice recrystallized. Efforts have been made to determine the dithionate by oxidation to sulphate in alkaline solution with hydrogen peroxide or bromine. Neither of these processes gave any quantitative oxidation. Oxidation with potassium chlorate and nitric acid did not take place quantitatively either. We therefore determined the concentration of the solutions by evaporation and drying over an argand-burner.

$K_2S_3O_6$. We tried to produce the salt by Willstätter's method,⁴ but this method only gave a small yield of an impure product. The salt used was produced by Raschig's method⁵ and recrystallized. By qualitative tests it proved to be free from thiosulphate and other polythionates. Quantitative determinations were undertaken by Kurtenacker and Bittner's method,⁶ with methyl-red as indicator. The finished product gave by analysis 100.5% potassium trithionate.

² J. Am. Chem. Soc., **43**, 1610 (1921).

³ Z. anal. Chem., **40**, 17 (1901).

⁴ Ber., **36**, 1831 (1903).

⁵ "Schwefel- und Stickstoffstudien," p. 296.

⁶ Z. anorg. Chem., **142**, 119 (1925).

$K_2S_4O_6$. Produced by Raschig's method⁷ and recrystallized; proved to be free from sulphite, thiosulphate, trithionate and pentathionate, but contained traces of sulphate. Quantitative determinations by Kurtenacker's method⁸ on the finished product gave 99.77%.

$K_2S_5O_6$. Produced by Raschig's method.⁹ Analytical method analogous to that which was applied to the tetrathionate. The resultant substance contains a considerable amount of potassium chloride, and it turned out to be impossible to remove this quantitatively without a further simultaneous extensive decomposition of the pentathionate. Having a number of times vainly tried to bring about a purification we decided (as the production of the pentathionate is rather protracted) to carry out the optical measurements on a solution which contained both salts. A solution of this kind was produced, analysed and its rotation measured. A definite quantity of potassium chloride was then added to a definite quantity of the solution, and the resultant solution was again analysed and the rotation measured. The molecular rotation of potassium pentathionate was established from these two determinations, and the rotation of the potassium chloride was eliminated by use of the rule of addition.

The figures quoted in the table show some examples of the importance of the constitution with regard to the magnetic rotation. It is, however, only the most outstanding features which will appear, and one dare not draw conclusions of a more extensive sort from this basis. The cause of this lies only in a lesser degree in the errors of measurement, which, as stated, amount to ca. 1% of the M-values. Of much greater importance is the alteration of the molecular rotation with the concentration which, as may be seen in the table, can in some cases amount to 10% of the value of the rotation. Figures of real value for the purposes of accurate comparison should therefore be provided by measuring each individual substance in a larger number of different concentrations and then extrapolate the results to infinite dilution. As far as material exists, M does not, however, in most cases seem to approach any limit within the concentrations which can be treated experimentally.

The following examples of the constitutional influence on the magnetic rotation have been taken from diluted solutions with approximately the same value for μ .

I. Addition of O.	ΔM	I. Addition of O.	ΔM
$H_2O_2 - H_2O$	0.1	$Na_2SO_4 - Na_2SO_3$	-2.7
$KOCN - KCN$	-0.9	$SO_2Cl_2 - SOCl_2$	-3.2

As the rotation of Na_2SO_4 has not been measured, this has been established from the rotation of $(NH_4)SO_4$, the difference $(NH_4)SO_4 - Na_2SO_4$ being taken as equal to the difference $(NH_4)_2S_2O_8 - Na_2S_2O_8$.

⁷ "S- und N-studien," p. 289.

⁸ Z. anorg. Chem., **134**, 265 (1924).

⁹ "S- und N-studien," p. 276.

II. Addition of S.	ΔM	II. Addition of S.	ΔM
$\text{Na}_2\text{S}_2\text{O}_3 - \text{Na}_2\text{SO}_3$	2.8	$\text{K}_2\text{S}_3\text{O}_6 - \text{K}_2\text{S}_2\text{O}_6$	3.7
$\text{K}_2\text{S}_5\text{O}_6 - \text{K}_2\text{S}_4\text{O}_6$	3.3	$\text{KSCN} - \text{KCN}$	5.0
$\text{K}_2\text{S}_4\text{O}_6 - \text{K}_2\text{S}_3\text{O}_6$	3.7		

The rotation of $\text{K}_2\text{S}_2\text{O}_6$ is calculated by means of the difference $\text{K}_2\text{S}_2\text{O}_3 - \text{Na}_2\text{S}_2\text{O}_3$. We observe the fact that the discrepancy in properties which are otherwise often found between the dithionic acid and the polythionic acids does not appear here. With regard to magnetic rotation the dithionic acid falls very nicely in line with the polythionic acids.

III. Substitution of O with S.	ΔM	III. Substitution of O with S.	ΔM
$\text{H}_2\text{S} - \text{H}_2\text{O}$	4.4	$\text{KSCN} - \text{KOCN}$	6.0
$(\text{NH}_4)_2\text{S}_2\text{O}_3 - (\text{NH}_4)_2\text{SO}_4$	5.5	$\text{CS}(\text{NH}_2)_2 - \text{CO}(\text{NH}_2)_2$	6.4

We thank the director of the laboratory, Prof. Dr. Julius Petersen, for his kind permission to use the means of the laboratory for this work.

*Chemical Laboratory A.
Royal Technical College, Copenhagen.
April 27, 1932.*

ADSORPTION AT CRYSTAL SOLUTION INTERFACES*

VI. Macroscopic Sodium Nitrate Crystals grown in the Presence of Dyes and Other Foreign Materials

BY L. A. WEINLAND, SR. AND W. G. FRANCE

Introduction

One of the major problems engaging the attention of colloid chemists is that of the stability of colloid systems. The factors bringing about and maintaining a more or less stable condition in sols have been studied attentively from all angles. Prominent among these factors has always been the phenomenon of adsorption. Since the term adsorption means a change in concentration at an interface, there is no reason for excluding from this study the important interfaces that exist between crystals and the solutions from which they develop. Especially is this true since it has been shown conclusively that many sols are made up of very finely dispersed particles of a definitely crystalline character. This fact has been established by work on X-ray analysis. Scherrer¹ and Haber² found by the use of the well-known powder method of X-ray analysis that dispersed gold showed the same lattice as macro-crystalline gold and that the particles of colloidal zinc sulfide were crystalline in character. This at once suggests that the study of crystal growth, and the various factors influencing the same, have an important bearing on stability.

The present investigation is an extension of the previous work carried out in this laboratory on "Adsorption at Crystal Solution Interfaces," and is concerned with the influence of foreign materials such as dyes, gelatin, and metal salts on the crystal habit of single macroscopic crystals of sodium nitrate.

For full details of methods used in this investigation as well as complete history and bibliography, reference is made to previous articles in this series.^{3,4,5,6,7,8,9}

* In part from the dissertation presented to the Graduate School of the Ohio State University, by L. A. Weinland, Sr., June 1930 in partial fulfillment of the requirement for the Ph.D. degree. Presented before the Division of Colloid Chemistry at the Cincinnati Meeting of the American Chemical Society, September, 1930.

¹ Nachr. Ges. Wiss. Göttingen, 1918, 96.

² Haber: Ber., 55B, 1730 (1922).

³ McBurney & France: J. Am. Chem. Soc., 46, 540-44 (1924).

⁴ Eckert & France: J. Am. Cer. Soc., 10, 579-91 (1927).

⁵ Keenan & France: J. Am. Cer. Soc., 821-27.

⁶ Bennett & France: J. Am. Cer. Soc., 11, 571-81 (1928).

⁷ France: Colloid Symposium Annual, 7, 59 (1930).

⁸ Lash & France: J. Phys. Chem., 34, 724-36 (1930).

⁹ Foote, Blake and France: J. Phys. Chem., 34, 2236-40 (1930).

Experimental Part

Sodium nitrate was chosen for study with reference to adsorption, modification of crystal habit, and growth ratios for the following reasons.

- (1) The crystals are relatively stable in air;
- (2) The crystallographic data are available;
- (3) Being rhombohedral a different form of symmetry is presented than in the previous work.

(4) Statements have appeared in the literature,¹⁰ to the effect that the modification in crystal form of sodium nitrate is due to strongly adsorbed anions. The statement is made that in the presence of nitric acid, because of the strong adsorption of anion, the crystal habit of sodium nitrate is changed. From this and other considerations Saylor believes that the modification of crystal habit by foreign substances may be predicted and that a general rule can be laid down covering all cases of modification by adsorption.

Ideas developed in previous papers of this series are not in accord with this assumption. It was, therefore, thought advisable to continue the study of sodium nitrate, applying the technique and methods used by previous workers in this laboratory.

A good grade of C.P. sodium nitrate was recrystallized once from water, the crystal mass dried and dissolved to make a solution saturated, or nearly so, at room temperature. This saturated solution was poured in a shallow layer in a large crystallizing dish and set away in a place free from temperature changes and air currents. As soon as crystals of sufficient size had formed these were picked out and dried between filter paper. It was later found that the presence of a very small amount of nitric acid (less than 1 per cent) not only fostered the growth of large crystals, but also prevented entirely the troublesome crusting at the surface of the solution and the extensive creeping up the side of the dish. These crystals were of the same composition as the ones grown in the absence of the acid and there was no modification in the crystal habit.

Short lengths of copper wire were sealed into one of the faces of the rhombohedral crystals of sodium nitrate. The wires carrying the crystals were thrust through thin sections of cork stoppers which were notched and fitted into small shell vials containing a saturated solution of sodium nitrate to which the foreign substance had been added.

It was observed that if the crystals were suspended and left in open vials, evaporation was too rapid and considerable distortion in shape occurred. This distortion took the form of enlarged bases and faces covered with ridges, stair-step like formations and attached meal from the surface of the solution. In order to control the growth the vials were placed in a large desiccator along with a three-inch crystallizing dish containing a small amount of concentrated sulfuric acid. In this way the influence of about thirty substances was determined. The results are given in Table I. The formulas for the series of dyes designated by number have previously been published by one of us.¹¹

¹⁰ Saylor: Colloid Symposium Monograph, 5, 49 (1928).

¹¹ France: Loc. cit.

TABLE I

Effect of Foreign Substances on Crystal Habit of Sodium Nitrate

Quinoline Yellow	Modification
Picric Acid	No modification
Diamine Sky Blue F.F.	Modification
Para Rosaniline	No modification
Ponceau Red	No modification
Fuchsin	No modification
Congo Red	No modification
Naphthol Yellow	No modification
Oxamine Blue	No modification
Gelatin	No modification
Bismarck Brown	Modification
No. 1	No modification
No. 4	Modification
Methylene Blue	No modification
No. 5	Modification
No. 6	No modification
No. 2	No modification
No. 8	No modification
No. 9	No modification
No. 13	No modification
No. 18	No modification

Note: Nos. 3, 7, 10, 11, 12, 15, 16, 17 were all insoluble in sodium nitrate solution. Nitrates of the following metals, lead, silver, mercurous and mercuric mercury, copper, cadmium, bismuth, cobalt, nickel, manganese, zinc, were all tried and found to be without effect.

Nature of Modification

In the few instances in which the crystal habit is modified at all, the modification is of the following nature: The regular faces of the rhombohedron continue to grow perpendicularly, while at the same time there appear at one or more corners of the crystal triangular truncations or octahedral faces. These are never present at the start but are induced artificially through the process of adsorption at these faces. This seems to indicate that a corner of a crystal may be looked upon as the probable locus of a face, but that in the regular processes of growth these faces grow so rapidly perpendicularly that they never attain to any more than a microscopic area. Adsorption slows up the rate of displacement of these faces and since the rate of perpendicular displacement of the regular faces is not interfered with, by the adsorption of the foreign substances, the octahedral faces must of necessity develop.

The displacement of these artificially developed faces relative to that of the regular faces of the rhombohedron was measured and expressed in terms of the growth ratio V_{111}/V_{100} . In previous measurements of growth ratios advantage was taken of the fact that the seed crystals were provided at the out-

set with all the required faces. However, with sodium nitrate cube faces only were initially present and therefore, the octahedral faces had to be developed before the measurements could be made.

This was accomplished by suspending carefully selected crystals in the saturated solution containing the desired concentration of foreign substance. When the octahedral faces appeared on the opposite corners of the suspended crystal it was then carefully orientated in the optical train so that a pair of

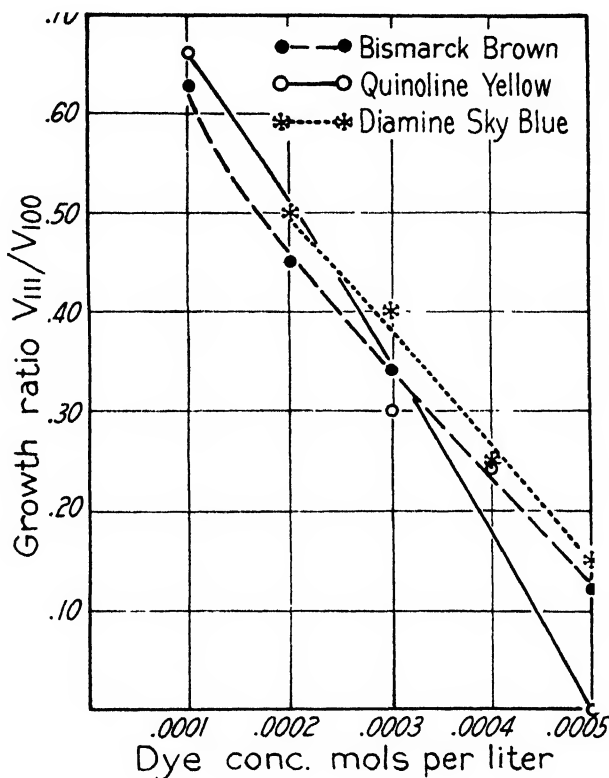


FIG. 1
Growth Ratio-Dye Concentration Curves

octahedral faces and a pair of the regular cube faces were directly in the path of the beam of light and sharply focused on the ground-glass finder. An exposure of the film was made every hour, the film removed and developed and measurements were made as fully described in previous papers.¹²

One notable change was made in the photographic process. The constant temperature box made of compo board described in previous publications was abandoned in favor of a constant temperature room large enough to contain all of the apparatus and the experimenter as well. The temperature of the room was held at 25°C. by means of a bank of lamps as a heating unit and

¹² France: Colloid Symposium Annual, 7, 59 (1930).

an automobile radiator through which cold water flowed, as a cooling device. The relays controlling these were actuated by means of a large toluene mercury system. Air was forced through the radiator by means of a fan which was turned off automatically when the lamps were turned on. A large oscillating fan, set behind the lamps, ran constantly and circulated the air in the room. The humidity was indicated by means of a Hare wet and dry bulb hydrometer and was controlled by means of two large shallow trays containing calcium chloride to which water was added as needed.

A summary of the growth ratio data for diamine sky blue, quinoline yellow and Bismarck brown is contained in Table II. Fig. 1 expresses these results graphically. Growth ratios using dyes No. 4 and No. 5 were not determined, due to the irregularity of the octahedral faces which developed in these cases.

TABLE II
Summary of Growth Ratio Data

Table number	Dye	Concentration in mols per liter	Ratio V_{111}/V_{100}
IV	Diamine Sky Blue	.0002	0.50
XIX	Diamine Sky Blue	.0003	0.40
XVIII	Diamine Sky Blue	.0004	0.25
XVII	Diamine Sky Blue	.0005	0.15
III	Quinoline Yellow	.0001	0.66
XX	Quinoline Yellow	.0003	0.30
XII	Quinoline Yellow	.0004	0.24
VIII	Quinoline Yellow	.0005	0.00
X	Bismarck Brown	.0001	0.62
XVI	Bismarck Brown	.0002	0.45
XV	Bismarck Brown	.0003	0.34
XIII	Bismarck Brown	.0005	0.12

X-ray Spectrographs: In order to determine if the adsorption of the dye by the sodium nitrate crystal produced any change in the lattice constant, X-ray spectrographs were made using the powder method. Powder scraped from the faces of a sodium nitrate crystal that was strongly colored by quinoline yellow was placed in one end of the capillary tube and the other filled with powdered pure sodium nitrate. Careful checking of the resulting film revealed the fact that there was no displacement of the lines on the two sides of the median line, and that therefore the lattice constant was unchanged by the adsorption process.

Ultrafiltration: Solutions of the various dyes in saturated alum and sodium nitrate solutions were subjected to the process of ultrafiltration using membranes of collodion. The filtered solutions were examined with the ultra microscope and found to contain relatively few colloidal aggregates. Crystals were grown in these solutions and it was found that exactly the same modification appeared as when unfiltered solutions were used.

Discussion of Results

The effect of those dyes modifying the crystal habit of sodium nitrate is such that faces not normally present are developed in the process of adsorption and growth. These appear as octahedral faces at the corners of the rhombohedron, (a) and (b) Fig. 2. An inspection of the figure, drawn from X-ray data,¹³ shows that the octahedral faces are populated by ions of like charge whereas the normally occurring cube faces are made up of mixtures of positive and negative ions. Due to the partial polarization of the residual

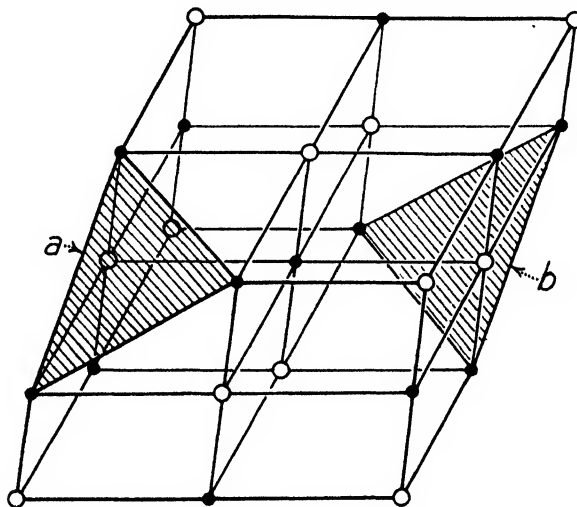


FIG. 2

Arrangement of Na^+ , (○) and NO_3^- , (●) ions in Sodium Nitrate rhombohedron

valencies in the latter one would expect the adsorptive effects to be greater at the octahedral faces. The fact that the dyes are preferentially adsorbed on these faces is in harmony with this view. Further support is given by the quantitative results obtained in the measurement of the growth ratios V_{111}/V_{100} . These values decrease from about 0.6 to 0.0 over a dye concentration range of from 0.0001 M to 0.0005 M. The reduction in the velocity of the perpendicular displacement of the octahedral faces together with the accompanying decrease in growth ratios resulting from the adsorption of the dye is in agreement with the conclusion reached in earlier work, that if a foreign material can be adsorbed by a growing crystal the adsorption will in general occur at those planes having the stronger fields of force. This would seem to indicate that one should be able to predict, on the basis of the lattice structure of a crystalline compound the possible variations in habit which would result from the adsorption of a given foreign substance.

One great difficulty which presents itself is that apparently there is no simple rule that enables one to predict just what foreign materials will be ad-

¹³ Wyckoff: "The Structure of Crystals," 1st Ed. 349 (1924).

sorbed by any one crystalline substance. While comparison of the formulas of those dyes which were adsorbed with those which were not is not especially helpful, such a comparison does, however, show that strongly polar groups are present in all cases where adsorption has occurred. Presumably such groups play an important part in the adsorption process.

The ultramicroscopic examinations and the ultrafiltration of the dye salt solutions appear to indicate that no relation exists between the action of the dyes in modifying the crystal habit and their colloidal state of dispersity.

The X-ray spectographs show that the lattice constant of sodium nitrate is not measurably changed by the adsorption of quinoline yellow. A similar result was obtained in previous work with potassium alum and diamine sky blue. These results indicate that the adsorption occurs interstitially rather than as individual planes or by the replacement of the ions of the unit cell. Further work is at present under way in order to determine the validity of this conclusion.

Buckley¹⁴ has made an extensive study of habit variation of crystals produced by slow and rapid crystallization and by added impurities. These impurities consisted for the most part of ions of the RO_4 and related types. His investigations involved the production of various crops of crystals and the classification of the individual crystals in each crop according to their habit variations. He concludes that the RO_4 and related ions which modify the habit of sodium chlorate do so by "taking the place of the ClO_3^- ions." This replacement is believed to be effected by means of the oxygen triangles of the ions. In comparing those ions which were effective with those which were not he comments as follows: "The effective ions by virtue of their shape and the orientation of their attractive force, are able to adhere, while the ineffective ions are probably unable to accommodate themselves to the environment, though in all likelihood, some distortion, compatible with surface adherence of the ion is permissible."

While the substances studied and the methods employed by Buckley are not strictly comparable to those of the present investigation it is nevertheless interesting that similar conclusions regarding the importance of the size and shape of the ions or molecules of the adsorbed materials are reached in both investigations.

Apparently in the absence of exact information concerning the size and shape of ions and molecules and the magnitude of the forces effective at the crystal solution interfaces it is unlikely that accurate predictions can be made, at the present time, as to just what substances any given crystal will adsorb.

Summary and Conclusions

The results obtained in this investigation lead to the following conclusions:

(1) The adsorption of the dyes by a growing crystal of sodium nitrate is dependent upon the residual valency force fields of the crystal face; the inter-

¹⁴ H. E. Buckley: *Z. Krist.*, **73**, 443 (1930); **75**, 15 (1930); **76**, 147 (1930); **78**, 412 (1930); **80**, 238 (1931); **81**, 157 (1932).

ionic distances within the crystal face; and the presence and distribution of polar groups in the adsorbed molecule or ion.

(2) The adsorption is selective for certain faces, namely those having the stronger fields of force.

(3) The adsorption results in a modification of the crystal habit and a reduction in the growth ratio V_{111}/V_{100} .

(4) With increasing concentration of dye the adsorption becomes greater and the V_{111}/V_{100} values become progressively smaller. This effect continues until a limiting concentration is reached at which the V_{111}/V_{100} value becomes zero and growth stops.

(5) The X-ray data indicate that the dye is adsorbed interstitially. If subsequent work proves this to be general, it will account in part at least for the comparatively small number of substances that are adsorbed by a growing crystal, since, in this event the adsorbed ions or molecules not only would have to possess the required polar properties to satisfy the adsorptive forces of the growing crystal, but would at the same time have to be of the right dimensions to fit into the interstices of the crystal lattice. The number of substances fulfilling both of these conditions simultaneously would naturally be small.

(6) Both the X-ray data and the composition of the dyes render Buckley's explanation for the modification of crystal habit by ions of the RO_4'' and related types inapplicable to the present work.

(7) The adsorption is independent of the colloidal dispersity of the dyes.

(8) These conclusions are in agreement with those arrived at in the earlier investigations of this series.

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THE TRANSFORMATION FROM ROSE TO GREEN MANGANOUS SULFIDE

BY HARRY B. WEISER AND W. O. MILLIGAN

The writers recently¹ criticised certain calculations and conclusions of Mickwitz and Landesen.² The validity of the calculations has been upheld by Landesen³ on the ground that a hydrochloric acid solution which was set down as " $N/10$ " in his Table I (reproduced as Table V in our paper) was not really " $N/10$." He points out that on page 110 of the paper of Mickwitz and Landesen the exact value was given. The data in question, which Landesen has designated as a "detailed statement" consist of the following: "Gehalt der ständigen Lösungen: 10 ccm $MnCl_2$ -Lösung 0.2744 g Mn; 10 ccm HCl-Lösung = 0.4437 g HCl, entsprechend 0.0273 g NH_3 ."

The data mean that the hydrochloric acid solution was 1.217 N . It appeared obvious to us that the solution referred to could not be the one designated in the tables as " $N/10$." In the light of Landesen's note it now appears that the so-called $N/10$ solution actually used had been prepared from this standard solution by dilution. However no statement regarding the dilution can be found in the original paper, but Landesen states in his note that the solution was used mostly in tenfold dilution, and therefore was not $N/10$. Accordingly the concentration of the acid in Table I should have read 0.1217 N instead of $N/10$. Landesen states that he called the 0.1217 N acid $N/10$ because of its "proximity" to $N/10$ and for "brevity." Any comment on these extraordinary reasons for designating 0.1217 N acid as $N/10$ would be superfluous.

In any event, the important point that we wished to make was that the conclusions of Mickwitz and Landesen are incorrect regardless of the correctness or incorrectness of the calculations. Thus we stated: "But even granting the presence of typographical errors that would account for the discrepancies noted above, the errors inherent in the experimental procedure of Mickwitz and Landesen are too great to enable one to conclude that there is one rose sulfide having the formula $H_2Mn_3S_4$ and one having the formula $(NH_4)-HMn_3S_4$."

Landesen also believes that we have stupidly or deliberately misinterpreted some of his statements. He claims that we intimated that Mickwitz and Landesen had "proved and concluded" that rose manganous sulfide will not turn green in the presence of alkali sulfide. What we actually said was: "Favorable conditions for obtaining the green sulfide have been described by a number of people. The experimental procedures were summarized and ana-

¹ J. Phys. Chem., **35**, 2330 (1931).

² Z. anorg. Chem., **131**, 101 (1923).

³ J. Phys. Chem., **36**, 2521 (1932).

lyzed critically a few years ago by Mickwitz and Landesen. As a result of this analysis and some observations of their own the following conclusions were reached: (1) The transformation from rose to green manganous sulfide never takes place when precipitation is effected with alkali sulfide . . ."

This statement of ours was based on the two following statements in the paper of Mickwitz and Landesen: "The sulfides of potassium and sodium precipitate a rose sulfide which does not go over to the green form."¹ "In the absence of free excess ammonia in the reaction mixture there is no transformation to the green modification from the rose manganous sulfide, freshly precipitated from manganous salt solution with ammonium sulfide."²

Landesen is correct in stating that Mickwitz and Landesen record no experiments of their own with sodium sulfide as precipitant; but no one stated that they did. However, in their proposed mechanism for the transformation from the rose to green forms, it is essential that free ammonia be present. Our only contention is that the presence of ammonia is not essential for this transformation, since we showed that the transformation takes place in the presence of sodium sulfide in the complete absence of ammonia, free or bound.

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¹ Mickwitz and Landesen: Loc. cit., p. 101.

² Mickwitz and Landesen: Loc. cit., p. 118.

THE USE OF AN ELECTRODE TO STUDY IRREVERSIBLE REACTIONS: THE POLYMERIZATION OF ACETALDEHYDE

BY VINCENT HNIZDA AND D. J. BROWN

Acetaldehyde in presence of acids, salts, and other compounds undergoes polymerization. It has been shown recently¹ that solutions of aldehydes may be used as electrodes showing the variation in voltage for the aldehyde that is formed for reversible electrodes. Hence, we should be able to follow the polymerization by observing the change of voltage of various solutions of acetaldehydes against a standard electrode the same as has been done with reversible electrodes.

The apparatus used and method of measuring was essentially that used by Arenson, Roller, and Brown, except that a Leeds and Northrup student type potentiometer was substituted for the type K, since the former was suitably accurate and could be more rapidly manipulated. All solutions were prepared and kept in absence of oxygen and light except that of ruby lights.

Perchloric acid was purified by distilling under reduced pressure in the presence of barium perchlorate. The distillate was diluted with water and boiled several times to remove nitrates and chlorides. Tests proved that this reduced sulfates and chlorides to less than .00001 normal. More dilute solutions were prepared by diluting with conductivity water, the oxygen removed by boiling under reduced pressure and again diluted to the original mark with "oxygen-free" conductivity water. The diluted solutions were checked with standard alkali solution.

Sulfuric acid, hydrochloric acid, potassium perchlorate, and potassium chloride solutions were prepared by using similar precautions.

The acetaldehyde was prepared by distilling paraldehyde acidified with phosphoric acid in a train of nitrogen. The acetaldehyde was redistilled and kept at 0° C. until used. The aldehyde solution was prepared by distilling under nitrogen the above acetaldehyde below 30°C. measured, diluted with "oxygen-free" conductivity water and kept at 0°C. The diluted solutions were checked by adding sodium sulfite and titrating the sodium hydroxide formed.²

The solutions were kept free from oxygen and when required, were forced with nitrogen free of oxygen into burets and then measured into the electrode chamber, and mixed rapidly by bubbling a rapid stream of nitrogen through the solution for one minute. To complete the liquid circuit with the standard electrode the solution immediately was forced into the bridge tube by mercury, which also acted as the metallic conductor. The first reading was observed within two or three minutes from the starting of the preparation of the mixture.

The value for "Equi." equilibrium, is the value obtained after standing 24-72 hours. No further change was observed.

The change of voltage for electrodes in which the molality of perchloric acid is greater than that of the acetaldehyde change similar to that of (a), but

¹ Arenson, Roller and Brown: *J. Phys. Chem.*, **30**, 620 (1926).

² Seyewitz and Bordwin: *Bull.*, (5) **33**, 1000.

is more positive. The addition of potassium perchlorate has no effect. The effect of sulfuric acid at higher concentrations than acetaldehyde gave results similar to (a).

Representative data for various acids are given here:

t	(a) .10m HClO ₄ .10m CH ₃ CHO	(b) .10m HCl .10m CH ₃ CHO	(c) .10m H ₂ SO ₄ .10m CH ₃ CHO	(d) .12m HClO ₄ .70m CH ₃ CHO	(e) .01m HClO ₄ 1.6m CH ₃ CHO
3'	+ .275 volts	+ .054	+ .252	+ .290	.335
5	.288	.050	.264	.299	.340
10	.286	.049	.269	.294	.328
15	.286	—	—	.283	.315
25	.285	—	.270	.274	.295
60	.284	.047	.259	.259	.283
100	.286	.047	.258	.236	.282
200	.287	—	.256	—	.267
Equi.	.289	.044	.224	.212	.243

Since all reactions were to be followed electrometrically it was necessary to make the measurements in presence of a conducting solution within the cell. To determine the effects of chlorides each solution was .010 molar perchloric acid and 1.60 molar acetaldehyde except (i) which duplicated (a) above.

t	(f) .010m HClO ₄ 1.60m CH ₃ CHO .00001m KCl	(g) .010m HClO ₄ 1.60m CH ₃ CHO .0001m KCl	(h) .010m HClO ₄ 1.60m CH ₃ CHO .001m KCl	(i) .1m HClO ₄ .1m CH ₃ CHO
2'	+ .270	+ .218	+ .159	+ .250
4	.277	.220	.157	.265
6	.283	.222	.156	—
9	.287	.220	.157	.270
14	.282	.212	.157	.275
27	.275	.206	.155	.277
80	.259	.198	.156	.280
160	.245	.169	.155	.283
Equi.	.223	.167	.141	.287
			(x)	.221
			(y)	.111

(x) Indicates that potassium chloride was added to make .001 m. Equilibrium was attained at once.

(y) Indicates that potassium chloride was increased to approximately .01 m. Equilibrium value was attained instantly.

The results indicate that:

1. The measurement of irreversible electrodes while reacting may serve as a tool in determining the course of reactions.
2. The hydrogen ion apparently has a preservative effect on acetaldehyde proportional to its concentration, in fact acts as if it formed a compound.
3. The chloride ion has the effect as if it catalyzed the acetaldehyde polymerization proportionally to its concentration.
4. The apparent equilibrium as indicated by the voltage varies considerably from those of reversible equilibrium relations. This may be due to the fact that the reverse reaction is not catalyzed or that we have no true equilibrium but a metastable condition.

NEW BOOKS

Applied Colloid Chemistry. General Theory. By Wilder D. Bancroft. Third edition. 21 × 15 cm; pp. ix + 544. New York: McGraw-Hill Book Company, 1932. Price: \$4.00. Eleven years after the publication of the first edition and six years after the second edition, this third revised and enlarged edition of Professor Bancroft's classic work appears with the same general arrangement of material under the following chapter headings: adsorption of gas or vapor by solid; chemical reactions; adsorption of vapor by liquid and of liquid and solid by solid and liquid; adsorption from solution; surface tension-Brownian movement; coalescence; preparation of colloidal solutions; properties of colloidal solutions; electrical properties of colloidal solutions; stability of colloidal solutions; gelatinous precipitates and jellies; emulsions and foams; non-aqueous colloidal solutions; fog; smoke; gases and solids in solids; and thickness of surface films.

Unlike most of the best known books on colloid chemistry, this one is written deliberately and without apology for those "who are interested in colloid chemistry as chemistry rather than as mathematical physics." But colloid scientists of every school will welcome this new edition of what has come to be regarded as a standard work.

The book is a remarkable one in many respects. In the first place it contains an extraordinarily large amount of information systematically and concisely arranged. In the second place, it furnishes the most critical survey of the field that is to be found in any book on this subject in any language. On almost every page a research problem is suggested outright or is hidden between the lines. Finally, with all its multiplicity of critical details, the book is readable and delightfully entertaining. This is because of the author's wide general knowledge, his unquenchable enthusiasm, his ready wit, and his frequent use of homely illustrations to emphasize a point. Few men are gifted with the ability to say and to imply so much in so few words.

Although the subject matter of the book is arranged logically and systematically, it is believed that the volume will be used more widely as a reference book than as a text book for undergraduates. In the reviewer's opinion, the open volume presents too formidable an appearance for a text book. Full pages of uniform printing follow one after another, broken only by an occasional table or figure. Even the references in smaller type which imparted variety to the pages of the earlier editions, have been collected together in the back of the present volume. It is believed that the introduction of numerous section and paragraph headings outlining the contents of the several chapters in bold face type, would enhance materially the appearance of the volume and would add greatly to its usefulness as a text.

In the preface to the first edition which has been reprinted in this book the author writes: "This volume on general theory should be followed by at least one volume on each of the following subjects: silicate industries; paints and varnishes; plastics; fibers and dyeing; photochemistry and photography; petroleum industries; ore flotation and allied subjects; foods and beverages; soils and crops; biology and medicine. Allowing a minimum of three years to a volume, it seems improbable that I shall write all of these single-handed. With the general theory of the subject once cleared up, there is no reason why the other volumes should not be written by people whose knowledge of the special subjects is much greater than my own." It is, of course, too much to expect that Professor Bancroft should complete the series single-handed; but the marked success of his "General Theory" leads us to hope that other volumes will be forthcoming in the not far distant future. However, if he should never write another book, the several editions of "Applied Colloid Chemistry—General Theory" will stand as the greatest single achievement of this generation in bringing the importance of colloid chemistry to the attention of American scientists and industrialists.

Harry B. Weiser

Die gruppentheoretische Methode in der Quantenmechanik. By B. L. van der Waerden. 25 × 17 cm; pp. vi + 158. Berlin: Julius Springer, 1932. Price 9 marks. In the new development of physical theory there has been evident a division of thought between two schools, which seems to be aesthetic rather than scientific. On the one hand there are those whose primary interest is in *things*, who accept any mathematical means, however clumsy, as good enough to lead to an understanding of the subtleties of nature; and on the other there are those whose real enjoyment of the new physics lies in its *form*, its connection with certain beautifully general mathematical ideas. We may compare the two schools, respectively, to those chess players who like to give checkmate with the help of a queen and two castles, and to those who are not content unless their game can produce the position of a chess problem. The present work is of the second type. The very general principles of the theory of groups can be applied to some of the elaborate and troublesome processes of quantum theory, and often make possible a comparatively simple treatment of what otherwise may lead to very complicated formulae.

The present reviewer was rather ignorant of the application of groups of the quantum theory, and approached the book in the hope of gaining a better insight into the connection, but it must be confessed that he was not successful. Though every step in the argument is clearly expressed and readily acceptable, yet at some unknown stage the thread is lost and one found oneself wandering in a maze of half-understood mysteries. The author's style of writing appeared so lucid that it was natural to blame one's stupidity, but a thorough re-reading twice and even three times failed to remove the misunderstanding and so the author must surely bear a part of the blame. What is probably the trouble may be illustrated by an example. We all remember as school boys those curiously improbable statements about numbers of apples, or the age of a man and his wife, which led to simultaneous equations. Such problems taught us to deal quite readily with equations such as $5x + 3y = 8$, but the next stage, in which we had to work with $ax + by = c$, was enormously more difficult. If one asked what a was, the answer was that it might be 5, but one was left with the feeling that if it really was 5 it was unfair of the teacher not to call it so all along. The truth of course is that we are all very resistant to general ideas, and only accept them when we have treated so many special cases that we are bored by them into making the generalisation. The trouble with the present book is that though the author does give a few examples, he does not give enough of them to bore us into grasping that there is a single underlying general idea. It seems likely that it is beyond human ingenuity to accomplish the task in such small compass as this book, for its 150 pages have not only to explain group theory, but also to develop the main points of the quantum theory itself.

In conclusion we may express the hope that the author will attempt the task again, but this time with the guiding help of some intelligent ignoramus. It is certainly possible to master the quantum theory without groups, and under these circumstances the ordinary physicist has neither time nor inclination to embark on a full study of general group theory, such as is to be found in works specially devoted to the subject, but would much profit by a work of the present type. The author seems to have all the qualifications for writing such a work, if only he can overcome his simple faith in the rapidity with which the reader can grasp the new train of ideas of group theory.

C. G. Darwin

Les Statistiques quantiques et leurs Applications. By Léon Brillouin 24 × 16 cm. pp. 404. Paris: Les Presses Universitaires de France, 1930. Price 125 francs. That combination of mechanical principles and the laws of probability which we call Statistical Mechanics owes its origin to the desire to explain the laws of Thermodynamics by means of the laws of Dynamics. Its founders were Clausius, Maxwell and Boltzmann. Its first enquiries were directed to the discovery of the way in which the particles of a molecular system will be distributed among the various conceivable positions and velocities at a given time, when the distribution has been given at some original time. Considerable success attended this enquiry for gaseous systems. The next problem to occupy the attention of investigators concerned the phases which succeed one another in a molecular system in the course of time. But the first explicit consideration of the problem which is the central theme of Gibbs' classical work is to be found in Boltzmann's papers. That problem concerns a

great number of systems of the same nature, an ensemble of systems, as Gibbs calls it, and their distribution in phase and the permanence or alteration of this distribution in the course of time. Thirty years ago Gibbs wrote in the preface to his "Elementary Principles in Statistical Mechanics"—"In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of Thermodynamics, of radiation and of the electrical manifestations which accompany the union of atoms." In those thirty years the Quantum theory has enriched the province of Mechanics with its special hypotheses, and in correspondence with this widening of our views classical Statistical Mechanics has grown into Quantum Statistics with definite triumphs already to its credit in the regions of enquiry where Gibbs found nothing but doubt and perplexity. A luminous and comprehensive account of this great forward stride will be found in the excellent treatise before us. Originally M. Brillouin wrote it as a volume for the well-known series of French works, "Conferences—Rapports de Documentation sur la Physique." Recently it has been translated into German and published as Number XIII of the excellent monographs published by Julius Springer under the common title: "Struktur der Materie."

In the first two chapters the author begins with the problem of full radiation carrying it as far as classical statistical methods will allow, i.e. to the displacement law of Wien. He signalises at this point the failure of the classical methods to reach the truth as known from experimental effects. "To determine the precise form of the law of radiation one must introduce an additional hypothesis. If the laws of mechanics and electromagnetism are rigorously applied to intra-atomic actions we arrive at the Rayleigh Law of radiation. But this is impossible in practice; the very existence of atoms rests on the new quantum laws and these laws carry with them as a corollary Planck's formula for full radiation."

At this point the author having shown the need for new hypotheses, proceeds in chapter III to develop the concept of the photon in conjunction with relativistic mechanics and the Planck constant. The chapter is devoted to a summary of Louis de Broglie's work and leads to an introduction of Heisenberg's principle of indeterminacy.

The succeeding chapter opens with the following remark. "We have summarised the current ideas concerning the structure of molecules and atoms and pointed out the important part which the 'quanta' play in this connection. We must return to the problem which was raised in the first chapters, namely the study of isothermal radiation. Originally the quanta were introduced by Planck for the purpose of interpreting the experimental laws for black bodies. The hypotheses of Planck were markedly different from those which we have expounded above. It seems indispensable therefore to verify that our point of view will lead us just as well to Planck's formula for radiation. For that purpose, we must recall certain fundamental notions relating to the statistical interpretation of thermodynamics. These definitions of probability were introduced by Gibbs and Boltzmann apropos continuous problems, that is to say concerning bodies or systems capable of passing during an evolution through an uninterrupted series of configurations each of which differs infinitely little from its predecessor and its successor. That is the case with all the usual mechanical systems. But with Bohr's atom we find ourselves faced with a very different problem, so it is necessary to undertake detailed definitions and precise statement of the manner of applying them." This chapter is therefore devoted to a statement of the general definitions of statistical thermodynamics, so framed that they can embrace all the problems of the classical period and still be wide enough to cover the subsequent development of quantum statistics. The notions of quantity of heat, equilibrium state, temperature, entropy, and statistical entropy based on probability are rapidly passed in review and in connection with the latter, the various ways open for the interpretation of "probability." Liouville's Theorem and the ergodic hypothesis lead to the introduction of the canonical ensemble of Gibbs as a basis for the calculation of the probability of states of a system at a given temperature, other than the most probable. This chapter includes an account of the methods of calculating mean values introduced by Darwin and Fowler and concludes with a summary of the formulae of classical thermodynamics and their statistical analogues.

The reader is now in a position to grasp the first innovation of the hypothesis of quanta in statistical calculations—the introduction of the finite elements of extension in phase, or

"cells" based on the magnitude of Planck's constant. Chapter V opens with the application of this idea to the stationary light waves which can exist in a reflecting enclosure and the connection between these and the quantised states of the associated photons. This is succeeded by the abandonment of Boltzmann's method of calculating probabilities which assumes that the molecules or ultimate particles of a system can be distinguished from one another; this naturally leads to the Bose-Einstein method where one assumes that any number of representative points may go into one cell, and to the Fermi-Dirac method in which a cell may contain one, but not more than one, representative point or none at all. The appropriate formulae for these two methods are developed, statistical and thermodynamical, and the significance of these results in the case of a degenerate gas is made clear. The connection of the Fermi-Dirac method with Pauli's exclusion principle is pointed out and the important bearing of the latter on the unexpectedly feeble paramagnetism of the usual metals. In the sixth chapter the original problem of the statistics of full radiation with which the book opened is once more taken up and exhaustively treated by means of the concept of the photon and the Bose-Einstein method of counting probabilities. Associated problems concerning fluctuation of energy in an enclosure, emission and absorption of light by an atom and the Compton effect are considered.

One of the most valuable features of the book is the very comprehensive treatment of the electron theory of metals which it contains. For many years the free electron theory has been under a deep cloud of suspicion. Its apparent failure to meet the most obvious requirements of experimental fact—e.g. its impotence in face of the now well-known phenomenon of superconductivity—had turned the minds of theorists to other hypotheses for a firm basis for a sound theory. However, a most remarkable change has come over the whole situation during the past five years since the advent of the Wave Mechanics. This new formulation of the mechanical properties of ultimate particles gives a definite support for the application of the Fermi statistical method to systems of electrons and protons. The distinctive feature of this method is the derivation of a distribution function which while agreeing with the usual Maxwell-Boltzmann function for ordinary conditions produces a remarkably different set of deductions for a "degenerate gas." The collection of free electrons in thermal motion in the milieu formed by the lattice of positive ions which is our physical picture of a metal is equivalent to a gas in a completely degenerate state and the appropriate treatment by the Fermi statistics has already dispelled many of the difficulties which we now see were really associated with the classical statistical method. It was not our physical model which was wrong; we were using inappropriate mechanical principles. In chapters VII and VIII of this book all this is explained in an extremely full and lucid manner. All the old troubles concerning the failure of the free electron theory to account for the values of the specific heats of metals vanish; the old calculations of Lorentz improved by these new ideas lead to quite satisfactory results concerning the thermal and electric conductivities. The Peltier, Thomson and Richardson effects, the contact potentials all show signs of fitting into an adequate theory. One important feature of the new method is the apparently paradoxical (on the old views) length of the free path of the electron. To this property around which keen discussion still centres a whole chapter is devoted.

The book concludes with a chapter on the "quantised atom" which contains among other material an account of the basis of those statistical calculations which are employed in discussing dissociation and the anomalous behaviour of electrolytes. There is in addition a mathematical appendix on special formulae and analysis used throughout the work.

J. Rice

Die Quantenstatistik und ihre Anwendung auf die Elektrodynamik der Metalle. By *Léon Brillouin*. 22 × 14 cm; pp. x + 530. Berlin: Julius Springer, 1931. Price. 43.80 marks, bound; 42 marks, unbound. The German edition differs from the French in a somewhat varied presentation of the hypothesis of photons in chapter III, and in the introduction into chapter VIII of some very recent work by the author on the free path phenomena.

It goes without saying that a book of this type cannot be read by anyone not possessing a sufficient mathematical equipment; and it seems to be almost a "fundamental postulate" that the "average" chemist does not possess that equipment; at least that is how the re-

viewer, who, however, is not a "chemist" in the conventional sense of the term, interprets the sort of conversation he hears in the company of chemists. He sincerely hopes that his interpretation is wrong; for as far as he can see the fundamental problem of the chemist and the physicist is the same; their experimental methods of approach are not merely complementary to one another; they actually in these days overlap in several ways. For the chemist to admit that he cannot for various reasons aspire to the mathematical equipment which the physicist finds he must now acquire is a counsel of despair. As Professor C. G. Darwin remarks in his "New Conceptions of Matter," a new subject "Mathematical Chemistry" is being born, and the chemist must of necessity learn the only language in which the laws and logical methods of an exact science can be expressed. Any chemist who seeks to understand what his own experimental work is revealing to him, must know something of the statistical methods now universally applied in all regions of research on ultimate properties of matter. The work before us will amply repay any effort involved in reading it. It will for instance equip him to follow the application of these new methods to the great problem of molecular combination; the situation there is still involved in difficulty, but there is no doubt that presently simplification will take place, but that simplification will not remove the necessity of knowing something of Quantum Statistics. In Professor Brillouin's work the reader will find all the lucidity of exposition so characteristic of the best French scientific writings.

J. Rice

Il Polarografo, sua teoria e applicazioni. By G. Semerano. 19 × 13 cm; pp. viii + 207. Padova: A. Draghi, 1932. Price: 16 lire. This book is a monograph on the dropping mercury cathode, in which the apparatus called the "polarograph" is described. The capillary electrode was originally used by Kucera for electrocapillary measurements analogous to the Lippmann electrometer method. Heyrovsky was the first to measure the current passing through the dropping mercury cathode, and showed that this furnishes a means for qualitative and quantitative analysis. In collaboration with M. Shikata of the Kyoto University he invented the Polarograph, which registers photographically the current-voltage curves, from the shape of which analytical deductions are drawn.

The intention of the author of the monograph is to furnish full information in the technique of polarography. Accordingly in the first part of the book the underlying electrochemical and physical principles are explained, including an original mathematical analysis of the current-voltage curves. Then the applications of the method in inorganic and organic analysis are described. Of analytical importance is the sensibility of the method which is able to estimate matter in the dilution of 10^{-6} gr. equivalents per litre, only a fraction of a cc. being necessary. The investigations of the problems of overvoltage, the mechanism of the dissociation of complex ions and of electro-adsorption at the cathode interface are described. Examples are also given of interest to physiologists, pharmacists and medical chemists. At the end of the book applications to industrial problems are mentioned, viz. in the chemistry of fermentation products, sugar and petroleum. A complete bibliography of 105 papers concludes this monograph, which contains many polarograms and diagrams. The whole subject developed to 1932 is treated exhaustively and the book makes interesting reading not only for those who wish to embark on polarographic research but also for all who are interested generally in electrochemistry.

J. Heyrovsky

Erratum

In the paper by John Frederick James Dippy (36, 2354), make the following changes:

p. 2356. The reproduction designated photograph 4 should be photograph 5 and that designated photograph 5 should be photograph 4. On the ninth line from the bottom change (6) to (b).

pp. 2357-8. The reproduction designated photomicrograph 1 (× 30) should be photomicrograph 2 (× 25) and that designated photomicrograph 2 (× 25) should be photomicrograph 1 (× 30).

THE PARTICLE SIZE OF BIOLOGICAL UNITS. A REVIEW

BY JOHN H. FERGUSON

The biologist has long been accustomed to render to the physical chemist a certain filial respect. This is born of an admiration for the logical method with which observations, carefully performed and accurately correlated, lead to tangible conclusions impressed with the stamp of finality by a successful and practical materialism. Granting the inadequacy of the materialistic viewpoint in the study of living things, it is, nevertheless, just this approach which has raised modern biology to the dignity of a science. The biologist, who has always admitted the handicap imposed by peculiar technical difficulties in controlling his variables—the *milieu* or *environment* as he chooses to term it—now finds the physicist and chemist discarding the old materialism and appealing to mathematics—subtle envoy of metaphysics—for a new “working hypothesis.” To let the matter rest on the mathematical formulation introduces an extraneous assumption of *belief*—a philosophical “faith,” which a material science has tacitly assumed,⁸⁰ pleading the justification not of strict logic but of utility or practical value.

This introductory digression is intended not to encumber the disputation of a scientific topic with the intangibilities of philosophy, but to temper the judgment of the exact sciences upon the methods and results of biological enquiry. The conclusions which are upheld by the faith of biologists rank equally with the “laws” of the material sciences. Every advance in the exact sciences is both a tool and an inspiration to the observer of living things. It is, therefore, both an honour and a privilege to address to physical chemists a consideration of certain data of some quantitative significance from fields of biology which border closely upon their own particular realm. These are fields in which the united physical and biological approach has yielded fruitful results by methods which are now offered for your considerate criticism. The topic is the particle size of such biological units as the filterable viruses, the bacteriophage of the Twort-d’Herelle phenomenon, and the genes which modern biology conceives to be the ultimate physical units of heredity.

It is emphasised that these are borderline cases and not as truly representative of biological phenomena as, let us say, the microscopically visible cell—whether animal, plant, or protist in origin. The problem of their size, therefore, is not synonymous with their claim to be regarded as “living,” and this distinction must be borne in mind to the conclusion of our argument.

The Filterable Viruses and Bacteriophage

In 1892, Iwanowski⁴⁵ found that the *Mosaic Disease* of tobacco could be transmitted in series by extracts of diseased leaves that had been filtered through bacteria-proof porcelain filters. The discovery was confirmed, independently, by Beijerinck,¹⁴ some seven years later.

It was in 1897 that Loeffler and Frosch⁵⁷ aroused the scientific world by the discovery that a similar "filtrate" from the blisters of *Foot-and-Mouth Disease* retains the full potency of the original infective material. No particulate matter could be detected in it by the microscope, or by staining the centrifugate. No visible growth occurred in a variety of culture media.

In 1915, Twort⁷⁷ noticed that some bacterial (*Staphylococcus*) colonies, isolated from a vaccination pock, underwent a destructive or lytic phenomenon, characterised by the appearance, in cultures on solid media, of translucent areas. These areas or "plaques" contained an agent which passed readily through the ordinary bacteriological filters and reproduced the phenomenon in series. It was dependent for its formation and activity upon the actual growth of the susceptible bacterium.

In 1917, d'Herelle³⁹ recorded a similar phenomenon in cultures of a dysentery bacillus (*Shiga*), broth cultures of which soon had their turbidity cleared up by incubating with a trace of the "filtrate" from the stools of a convalescent patient. d'Herelle has studied the problem, which he has named *Bacteriophagy*, from every angle^{37,38}. He has accumulated a large body of data and drawn many conclusions, some of which have aroused considerable controversy.

The hypothesis that the bacteriophage (the question of its plurality need not concern us here) is of a similar nature to the so-called "filterable viruses" is well grounded, and we may conveniently consider them together. Rivers⁷¹ lists some seventy diseases said to be caused by "filterable viruses."

Several conclusions relevant to our present theme now warrant general acceptance. The self-perpetuating agents are exceedingly small. They may be active in dilutions as high as 1:10,000 million. They often pass through high-grade bacteria-proof filters. They are invisible, or at least unresolved, even with a dark-ground microscope which is able clearly to resolve particles of the order of 250 millimicra in diameter.

Nevertheless, they must be regarded as *particulate*. There is a limit of dilution beyond which they do not infect. This cannot be explained away as an insufficiency of dosage, for if, say a cc of a bacteriophagic filtrate is within this limit of dilution, it will dissolve bacteria in a broth culture of any volume—9, 99, or 999 cc, it does not matter which (Gratia and de Kruif³³). Highly infective virus—or 'phage-containing fluids usually pass through the ordinary bacteriological filters, but not through the finest, such as the higher grade of the Chamberland bougies. Neither do they dialyse through alcohol-ether colloidion membranes which permit the passage of water, crystalloids, and certain highly dispersed colloids such as litmus blue.

The formation of isolated "plaques" or bacteriophage is also indicative of a dispersoid nature (d'Herelle,³⁸ Eijkman²⁷). A suspension containing 10,000 million 'phage corpuscles per cc—a "corpuscle" (d'Herelle) being defined as the least quantity which will carry on the phenomena of bacteriophagy—is quite limpid, like the water which forms the continuous phase. It shows, however, the Tyndall phenomenon. In short, we are dealing with matter in the *Colloidal State*, and, in view of the great advances in recent years in the science of colloid chemistry, it is fitting at this time to review our data relating to the

probable size of these "living" colloids. We use the term "living" with the diffidence expressed in an earlier paragraph.

The data about to be summarised indicate a *range* of particle sizes of the order of 20–100 $m\mu$, and they have been arrived at by methods which fall into three categories:

1. *Optical Methods*—Especially ultramicroscopy, and the method of photomicrography with very short wave-lengths of "light."
2. *Bacteriological Filtration*—Especially ultrafiltration through collodion gel membranes.
3. *Centrifugation*—As yet little developed in this field.

The Ultramicroscopy of the Filterable Viruses

The applied optics which enters into the theoretical consideration of the possibilities of microscopic technique is largely outside the scope of the present paper. Barnard⁴ may be quoted, however, for the following brief résumé of the basic principles:

"Microscopic objects may be divided into two classes, those that are seen by transmitted light, and those that can be made self-luminous. The former are seen as the result of partial or of selective light absorption, that is, they may be semi-opaque, the elements of structure absorbing more or less light, or they may be seen in colour as the result of selective absorption as seen in a stained preparation. For the object to be self-luminous it must be illuminated in such a manner that no direct light reaches the micro-objective, but only that which is refracted, diffracted, or scattered by the object itself. Under these conditions the method is known as dark-ground illumination."

Both methods are subject to the same limitations, which are due to (1) the relative opacity or refractivity of the object and the medium in which it is suspended, and (2) the "resolving power" of the optical system. *Resolution* depends upon the microscopic objective—which has now reached the limit of technical achievement in lenses* of N.A. 1.40—and also upon the wave-length of the light used. With ordinary visible light (average wave-length 550 $m\mu$) the "limit of resolution" is reached with objects of 0.2–0.25 micra in diameter. Of course much smaller particles down to 5 or 10 millimicra, or even less⁸² may be discerned by ultramicroscopy (Siedentopf and Zsigmondy, 1903⁷²), but here we are dealing with "diffraction images" which do not tell us much about the real nature and size of these sub-resolvable objects. Thus, d'Herelle³⁷ describes dark-field observations of particles entering the bacterial cell and increasing in numbers when bacteriophagy occurs; but these are not critical observations.

Provided that the increased magnification does not involve an appreciable loss of definition, a slight gain may be expected from enlarging the image by means of high-powered eyepieces. The new trend in microscopy is to employ the short ultraviolet wave-lengths of *light* in conjunction with quartz lenses

*This is surpassed in mono-bromo-naphthalene lenses.

and a suitable photographic method. The technical details are elaborate and the apparatus is very costly and difficult to use in actual practice. Barnard^{4,5} has secured good instruments for working with filtered ultraviolet wave-lengths of 275, 257 and 232 m μ . When the object can be protected against Brownian and the other movement (as in special slide cultures) for a sufficient length of exposure, photographs showing good resolution down to diameters of 50–100 millimicra may be obtained. Working with Gye⁴ and others,⁵ Barnard has photographed various viruses and bacteria. The aetiological organism of *Bovine-Pleuro-pneumonia*, which is probably the smallest micro-organism definitely seen and cultured, shows a mature "spheroid form," averaging 200–250 m μ in diameter, which buds off young "granular forms" of about half this size. This granular phase is a "filter-passer" (v. infra).

It is claimed that similar, but rather smaller, say, 75 m μ , spheroids and granules represent the causative viruses of the Rous chicken sarcoma, a mouse sarcoma, and even of human carcinoma. The inability of other investigators to confirm these results, especially when more rigid controls are made of the so-called "accessory factor," which is said to be present in ultrafiltrates of the diseased tissue and to be essential for the activity of the "virus," leaves us in doubt as to the true nature of the bodies which Barnard has photographed. Until the crucial experiment has been performed the matter must still remain *sub judice*.

It is of interest to note that recent work lends support to the idea that filterable forms may occur as phases in the life-history of a number of visible micro-organisms, the bacillus of influenza, for instance.

There is a definite limit to the use of short wave-lengths for ultramicroscopy. Just as the shorter wave-lengths of light are extinguished in a fog whereas the longer wave-lengths (the red of a *Neon* sign, for instance) get through, so, too, the use of short wave-lengths in microscopy is limited by the scattering of light by the molecules which make up the lens system, and the refraction image becomes faint and blurred and finally cannot be obtained.

Staining Methods—A priori, would seem to be futile when we can not even see the objects we wish to stain, and, in any case, great caution must be exercised in view of the ease with which one may obtain such artefacts as stain aggregates, protein flocculates, and the like. Two observations may be noted, however. By mordanting and then overstaining with *Giemsa's* stain, fine "granules" may be brought out in certain of the *cell-inclusions* which characterise a number of virus diseases (e.g., Ledingham,⁵⁴ 1931). There have also been described peculiar "Globoid bodies" in virus-containing filtrates, whereas controls do not show the same appearances. Bechhold and Villa¹² (1925) describe a special method of impregnation with successive layers of gold sols ("gilding") which is claimed to reveal even the micellae of serum proteins. Bacteriophage (*B. Coli*) "particles" were estimated by comparative data to have a diameter of greater than 35 m μ and less than 100–200 m μ . Interesting as these results are, they must at present be accepted with reserve.

From the lack of turbidity of 'phage containing filtrates as compared with the well-known milkiness of bacterial cultures (*B. Dysenteriae*) in fluid media von Angerer² (1924) computes for bacteriophage a diameter of less than 20-30 m μ .

Filtration Techniques

Since the method of ultra-filtration, in spite of all its difficulties, has been relied upon more than any other single method for determining the particle size of viruses and bacteriophage, we may allude to the variables *known* to be involved, and the methods whereby they may be controlled.

As with all biological experiments full *controls* must be run throughout. Protocols should include details concerning *animals, cultures, and media* used: also *apparatus*, and methods of *sterilization*. Sterilizing methods include: (i) aseptic method of preparation, (ii) especially in conjunction with an ultra-violet light chamber (Elford²⁸), (iii) autoclaving in alcohol-vapour, which tends to alter the permeability of the membrane, (iv) hot-air sterilization for metal parts, etc.

The Membrane: (a) Composition—is usually acetic-collodion (Bechhold,⁹ 1906), or, in Elford's³⁰ recent formulae (1931), the 'gel' which is deposited by amyl alcohol from an ether-alcohol-acetone solution of nitro-cellulose in such a way as to preserve the "orientation" which gives to ether-alcohol collodion membranes the high grade of uniformity they are known to possess. The lower the percentage of collodion the higher the permeability. Ordinary ether-alcohol collodion membranes are unsuitable because they are quite impervious to viruses and bacteriophage. The siliceous bacteriological filters such as the Chamberland, Berkefeld, Mandler, Seitz, etc. (Mudd⁶⁶) are not sufficiently uniform.

(b) Thickness—should be standardized by a suitable method of depositing layer by layer, or by a roller device such as that of Elford²⁸ (1929).

(c) Pore-size (average)—may be determined from the permeability to water or to air under pressure. The formulae used for the calculation invoke Poiseuille's law for the flow of fluids through minute channels such as pores or capillaries; (Bechhold,^{10,11} Bartell,⁶ Hitchcock,⁴² Bjerrum and Manegold,¹⁸ and Elford²⁸).

(d) Electrical-charge on membrane—may be estimated from its adsorption powers for a range of filterable dyestuffs in buffered solutions.

The Suspension: (a) Electrical charge on the suspended particles can be estimated by cataphoresis (von Angerer,² Olitzky and Boëz⁶⁸). The filtration should be conducted with buffered solutions in which the particles have the same sign as the membrane charge so that electro-adsorption is reduced to a minimum. The iso-electric point of foot-and-mouth disease virus, by cataphoretic measurements, is at pH = 8.0, and collodion membranes are negatively charged. Hence an alkaline reaction, pH = 8.5 \pm , is advocated (Olitzky and Boëz⁶⁸).

(b) The Medium in which the particles are suspended is important owing to (1) adsorption and (2) surface tension. Bronfenbrenner²⁸ showed that a col-

lodion membrane just impervious to bacteriophage would let it through if washed with broth, but not if washed with saline or a buffered phosphate solution of the same pH as the broth. Elford's²⁸ method of adjusting the protein content of all suspensions by dilution and the addition of horse serum, has something to recommend it.

(c) The Purity of the particulate agent itself, is a knotty problem, which for all practical purposes must be considered insoluble. There must always be traces of medium, cell-debris, and the like, adsorbed to the particles we are studying. Nevertheless, certain methods of purification which employ cataphoresis in addition to ultrafiltration (Bronfenbrenner²⁵) or diffusion into agar (Krueger's modification⁵⁸ of Arnold's³ method) have yielded "purified" bacteriophage preparations free from all traces of protein according to chemical and biological (immunological) tests. The trace of nitrogen still present in Krueger's material is about twice that of the culture medium. Most investigators in the present field have been content to use non-purified material with just a rough preliminary filtration through the coarser ("preliminary") grades of bacteriological filters.

(d) The actual Concentration of the agent we are dealing with, is obviously a matter of conjecture. For bacteriophage we have several methods of comparative determinations, *viz.*, (1) the "serial dilution" method; (2) the "plaque count"; and (3) Krueger's new method,⁵⁸ depending upon the time taken to reduce the turbidity of standardized bacterial suspensions to a pre-determined standard. (A limit of error of $\pm 3-5\%$ is claimed for this method.) For viruses we have only the very inaccurate method of the minimal infective dose.

The Actual Conditions of Filtration must be strictly uniform.

(a) The Temperature must be constant.

(b) The Time Factor must be controlled, for some organisms, given time enough, may actually grow through bacteriological filters, while others such as the spirochaetes may wriggle through.

(c) The Volume of Filtrate should not be more than a few cubic centimetres. There are always a few "pores" in the membrane which are considerably larger than the "average pore-size," and the greater the amount of filtrate the more chance there is of a stray particle getting through.

(d) Filtration Pressure is very important. Preliminary tests will indicate what pressure each grade of membrane will withstand (Elford²⁸). Always work well within this limit, usually not employing pressures higher than a few centimeters of mercury. Zinsser and Tang's⁸¹ method of noting the permeability to water both *before* and *after* the actual filtration affords a good and simple method of testing the integrity of the membrane.

The Results

Elford⁸⁰ has perfected his membranes to a sufficient extent to be able to rely upon their estimated "pore-size" as an index of the size of particles filtering through. Most other results, however, depend upon comparisons with colloidal solutions of known particle size. Now that the methods of determining such particle sizes have been greatly improved, these "standards" would ap-

pear to offer a real value if full attention is given to the electrical charge and other adsorption factors when the actual comparisons are made. The complete fulfillment of all the experimental controls we have outlined as an ideal which, although practicable, has not been realized, albeit one or two workers^{30,68} have come very near to it. The appended text-figure shows the agreement between the results of a number of authors quoted either because of the excellence of their technique or because of the historical sequence. Additional references are to be found in the bibliography. The data point to a *range* of particle sizes between 20 m μ and 100+ m μ , with the "granules" of the organism of bovine pleuro-pneumonia at the upper end, and bacteriophage at the lower. Some observers think that bacteriophage is even smaller than 20 m μ . Krueger,⁶² in particular, finds that his "purified" 'phage passes through 4.5–5.0% membranes, (as compared with 1.5–3.0% membranes which are the usual limit for 'phage and viruses). He estimates its size at about 5 millimicra.

Some of the data in the literature may be too low because of "leaky" filters. Other figures are too high because the particles are not sufficiently freed from gross impurities. Adsorption to cellular debris is the probable explanation of the non-filterability of such viruses as rabies, vaccinia, chicken-pox, and herpetic encephalitis. It is not always a mere question of size.

Sedimentation Experiments

Apart from the concentration of adsorbed viruses (like vaccinia) by centrifugation at, say, 6000–9000 r.p.m.,¹⁹ the ordinary speeds of centrifugation employed in the bacteriological laboratory are inadequate to alter the distribution of viruses or bacteriophage in "filtered" suspensions. The only positive results from sedimentation experiments are those of d'Herelle,³⁸ who found that a bacteriophage for a *Dysentery Bacillus*, when allowed to stand for 11 months, became ten times more concentrated in the bottom layers than on top. Using a Jouan centrifuge at 12,000 r.p.m. for half an hour, he found that a suspension containing at the outset some 1750 millions per cc of 'phage "corpuscles" (v. supra), resolved itself into an uppermost layer of 50 millions and a lowermost layer of 3700 millions per cc. He was unable completely to free the upper layers of 'phage corpuscles, and his results have not been confirmed.

The Size of Genes

It is the triumph of modern genetics to have adduced powerful evidence to show that the hereditary transmission of units of physical character is bound up with the behaviour of microscopically visible cell structures, especially the *Chromosomes*⁷⁵ into which the nuclear chromatin condenses during cell division. It has been found from breeding experiments that character units do not distribute themselves merely by "free assortment," as the original conception of Mendel⁶⁹ (1865) presupposed. Bateson and Punnett⁷ (1906) showed, in the sweet pea, that characters tend to remain together, "linked" into a number of distinct groups. The fruit-fly (or vinegar fly), *Drosophila Melanogaster*, has proved a remarkably valuable object for breeding experiments. Morgan and

his co-workers^{20,65,74} examined some 20,000,000 of these flies, all with carefully noted pedigrees. They discovered some 400 "mutants," i.e., new types of individuals with one or more altered genetic or hereditarily transmissible characters. These characters can be paired off into alternatives or "allelomorphs." They fall into just four *linkage groups*, and it is highly significant that each cell of *Drosophila* during its division contains four pairs of chromosomes, that is, four of maternal and four of paternal origin. In the mature germ and sperm cells, by a process of "reduction division," the chromosomes are reduced to four in number—the halved or *haploid* number. By observations on specimens which chance to have one of the chromosomes missing, it is easy to determine which chromosomes correspond to each linkage group. The group of characters associated with the sex chromosome is an especially profitable field of study. This linkage group contains some 150 characters in *Drosophila melanogaster*.

To the rule of "linkage" there is an important exception termed *crossing-over*.⁷⁴ Thus, in mating a yellow-wing + white-eye female fruit fly to a "wild-type" male with gray-wings + red-eyes, all the daughters are found to have gray-wings + red-eyes, and all the sons have yellow-wings + white-eyes. If these are inbred, 98.5% of the offspring (F_2) are like the grandparents, i.e., they have either yellow-wings + white-eyes or gray-wings + red-eyes. We have, therefore, two "allelomorphic (alternative) linkage groups, yellow-wing + white-eye and gray-wing + red-eye. However, 1.5% of the offspring of the second (F_2) generation have either yellow-wings + red-eyes or gray-wings + white-eyes. In these the linked characters are said to have "crossed-over." Crossing-over usually takes place in "blocks" because the character-units tend to stick together. The frequency with which a character tends to cross-over was shown by Sturtevant⁷⁴ to give an index of its closeness to other characters in the same linkage group with which the frequencies can be compared. Each "genetic unit" may be considered to have a definite "locus" on its chromosome, and the different "loci" form a linear chain for which a *map* may be constructed from frequency-of-crossing-over data. The least frequent crossing-over represents the nearest thing to the ultimate genetic unit now known as the *Gene*⁶³—and is provisionally estimated (Muller,⁶⁵ Morgan⁶¹), as one-fifth of Sturtevant's "genetic units," but it may be considerably smaller than this. Assuming that the "genes" are of equal size and evenly distributed along the "gene-string" (or chromosome), tentative and rather crude computations of the upper limit of their size may be made, in several ways, as suggested by Morgan in his Croonian lecture of 1922.⁶¹

By computing, from fixed and stained sections, the average volume of the head of the spermatozoön of *Drosophila melanogaster*, Morgan presumed that (this might be taken as a very rough approximation to the total volume of the 4 chromosomes (haploid number) it contained. Crossing-over data suggested $5 \times$ the known number of genetic units as a conservative estimate of the total number of genes present. It is justifiable to assert from these data that the genes (if assumed to be evenly distributed) are not larger than 77 $m\mu$ in diameter.

The chromosomes, when measured at the "metaphase" of mitotic-division, have fairly uniform width of about 0.2μ and respective lengths of 1.8μ (I), 2.5μ (II), 3.0μ (III), 0.2μ (IV), totalling 7.5μ in all. Their (cylindrical) volume is therefore $0.236\mu^3$. Dividing by the number of genes (2000, v. supra), and computing the gene diameter, we get a value of $60\text{ m}\mu$.

A still simpler method is to assume that the fully stretched-out chromosome of the "thin-thread stage" of conjugation during cell-division has all its component genes arranged end-to-end. In the case of Chromosome II, this chromosome length may be taken as 11μ . Some 110 genetic units are known to be associated with this chromosome, and we may take $5 \times$ this number as an estimate of the number of genes. If each gene takes up an equal fraction of the "gene-string" the width should occupy about $20\text{ m}\mu$.

A figure of $65\text{ m}\mu$ is obtained if the chromosome volume is used, the data being given in the second method.*

Many of the assumptions involved in the foregoing calculations are unwarranted, but the error is always on the upper side. A diameter of $20\text{--}80\text{ m}\mu$ may, therefore, be accepted as a limiting value definitely above the *gene* size. How far below this limit the gene may be still remains for future elucidation.

More recent cytological data have accrued from measurements of the *chromomeres*, or chromatin aggregates into which the chromosomes of some species are definitely subdivided. Belling¹⁵ has recently photographed the tiny chromomeres of the *Lily*. They average $0.5\text{--}0.1\mu$ (or less) across. At the limits of microscopic visibility, with unusually powerful instruments, he discerns a single central dot in each chromosome. This dot is probably less than 0.1μ in diameter. The possibility that this "central dot" is the "locus" if a single gene is a possibility, but is rendered unlikely by data (from other species) which indicate a much smaller number of chromomeres than of hereditary units.

Conclusion

Our data concerning the size of the biological units which we have considered are peculiarly difficult to weave into a definite conclusion. On the whole, they are somewhat too large to reconcile with physico-chemical data concerning the size of the largest known (or suspected) molecules. The lowest estimates of bacteriophage size ($5\text{ m}\mu$) are close to Svedberg's⁷⁶ values for the haemoglobin molecule. An average figure of $50\text{ m}\mu$ in diameter for our biological entities means a volume of a thousand times as great, with room for many hundreds of molecules the size of proteins. The conception of a self-perpetuating catalyst of molecular (? protein) size is an alluring prospect to the materialist in search of the "*Protyle*" of life. Speculation is fruitless, however, until such entities are definitely established by physico-chemical data on the one hand, while the biologist from his viewpoint recognizes their "vital" powers of reproduction, assimilation, and adaptation. It is perhaps insufficiently stressed that genetic phenomena (viewed in their evolutionary significance) are criteria of the "living" which diverge considerably from the

*Author's calculation.

Authority	Date	Biological Agent	Estimated Size	Compared with:	Method
Olitzky & Boëz	1927	Virus of Foot and Mouth Disease	20-100 m μ	Arsenic trisulphide (100 m μ)	Ultrafiltration (collodion)
				Collargol (20 m μ)	
				Haemoglobin (30 m μ) Blue litmus (1.8 m μ)	
Zinsser & Tang	1927	Bacteriophage for Staphylococcus Rous chicken sar- coma virus Herpes virus	20-100 m μ	Arsenic trisulphide	Ultrafiltration (collodion)
				Collargol	
				Egg albumin Casein Trypsin (impure)	
Prausnitz	1922	Bacteriophage for B. Dysenteriae	20 m μ	Collargol	Ultrafiltration (Haën)
				Haemoglobin	
				Gelatine	
d'Herelle	1918	Bacteriophage	20-30 m μ	Serum globulin	Ultrafiltration (collodion)

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Footnote

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THE PHYSICAL STRUCTURE OF ELASTIC COLLOIDS

BY W. F. BUSSE

Introduction

Gelatine, rubber, polystyrene, polyesters, soap, chloroprene, etc., differ widely in chemical properties, but they have one outstanding physical property in common—under the proper condition their limits of elastic deformation are enormously higher than those of any similarly shaped crystalline material. Efforts to discover by chemical methods the cause of this high elasticity have not been particularly successful, though they have shown that linear polymers of sufficiently great molecular weights are often highly elastic. The attempts to find a physical explanation of the elasticity in some cases have been partially successful, but no thoroughly satisfactory theory is available.¹⁻⁹ The physical theories which have been proposed range from one which assumes the presence of tiny gas bubbles in the material to others which postulate a two-phase brushwork structure, or which assume the existence of helical molecules that act as tiny springs. Although some of these physical theories are satisfactory in limited fields, they usually are not valid for any wide range of materials, and difficulties are often encountered in applying them to a new field. This is illustrated by the attempt to account for the elasticity of rubber on the basis of the two-phase theory of the structure of gelatine gels.⁸

In this paper the mechanics of the process of elastic deformation is analyzed in the attempt to discover the fundamental general conditions which are necessary and sufficient to produce a high degree of elasticity in any material, and to formulate these factors as precisely as possible. The result is an explanation which appears to be more general and comprehensive than previous theories. It is shown that the factors which explain the high elasticity (*i.e.*, the great extensibility and recovery) will also account for other properties such as swelling in solvents, hysteresis, elastic after-effects, etc., which often accompany high elasticity. While specific chemical properties of individual systems are not considered in this analysis, the theory of the physical factors responsible for elasticity is quite helpful in suggesting physico-chemical methods of modifying the properties of various elastic systems. One result of this study has been the production of fibrous and cellophane-like rubbers with rather unusual properties.

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Concepts included in the Term Molecule

In considering the structure of elastic colloidal materials, the gross physical properties are usually explained in terms of the properties of the primary units, or molecules. This, however, leads to confusion unless the various concepts included in the term molecule are clearly differentiated. An analysis of this term along the lines indicated by Bridgman¹⁰ would be of great help in this field, and it is to be hoped that someone will carry it out.

For purposes of this discussion at least three concepts or three types of units which are more or less vaguely included in the term molecule are recognized. The first is the chemical molecule, which is defined as the smallest unit possessing the chemical properties exhibited by a large mass of the material. In this sense the chemist requires the molecules of acetylene, benzene, acetic acid and salt to be written C_2H_2 , C_6H_6 , CH_3COOH , and $NaCl$, respectively. These formulas are usually consistent with the common ideas of valence; organic chemists, therefore, sometimes define a molecule as a group of atoms held together by primary valence bonds. Under this latter definition, however, any perfect diamond must be regarded as a carbon molecule, and the so-called molecular compounds are excluded. For practical purposes—*i.e.*, for writing equations—the chemical molecules of solid elements such as iron, sodium, carbon, etc. are considered as single atoms, and the molecules of solid compounds are the smallest groups of atoms that possess the observed ratios of the elements in them, making the copper sulfate molecule $CuSO_4 \cdot 5H_2O$, the iron carbide molecule Fe_3C , etc.

A second concept included in the word molecule may be called the physical molecule. This unit will acquire from thermal vibrations an average of $1/2$ kT ergs of energy for each of three translational degrees of freedom, neglecting quantum restrictions. It is sometimes identical with the chemical molecule, especially in the gaseous state, and the chemist uses this concept of a molecule when he writes the molecules of common gases as H_2 , N_2 , O_2 , Cl_2 and when he uses the weight, in grams, of 22.4 liters of a material in the gaseous state under standard conditions as the gram molecular weight. However, physical molecules also include such units as H , He_2^+ , CH_3 , which, though not very stable, can be recognized from band spectra; the particles of gold or mastic in colloidal solutions are also good examples of physical molecules. The sizes and weights of the physical molecules of a substance may change with temperature, rate of shear, and other factors, thus differing from the chemical molecules which, by definition, are invariants for a given substance.

When molecular weights are determined by cryoscopic or ebullioscopic methods it is the average weight of the physical molecules which is obtained. When this weight is not consistent with the chemical formulas, special assumptions such as association, ionization or solvation are made to explain the results without always recognizing that several different concepts of molecules are involved. In general, the molecule of the organic chemist is both the physical and the chemical molecule, and cryoscopic methods may, therefore, be used to

¹⁰ "Logic of Modern Physics" (1927).

determine chemical molecular weights. If there is a discrepancy between the chemical and physical molecules, however, as in the case of acetic acid in a benzene solution, the organic chemist considers only the chemical molecules.

The distinction between physical and chemical molecules has been emphasized before, but the use of these concepts interchangeably still causes confusion in our thinking and discussions. This is particularly apparent in the field of colloids where the distinction between the two concepts is more important as well as more difficult to make, and because a third concept has crept into use which should be distinguished from the first two. When Einstein's equation is used to determine molecular weights by viscosity methods a third concept is introduced into the term molecule and in some cases a new unit is measured. This is a mechanical unit, the group of atoms which hold together when the material is subject to a shearing stress. To show its relation to the other units and to emphasize the broadness of the accepted usage of the term molecule, this unit will be called a "mechanical molecule."

The value of this concept is brought out in the case of compounds which form normal solutions in one solvent while in another they form gels even at very low concentrations. Viscosity measurements of these solutions do not reveal much about the chemical molecules, though they may indicate the size of the mechanical molecules.

In gases and possibly in most liquids the physical and the mechanical molecules are identical; in liquids such as mercury, some of the mechanical molecules probably are also chemical molecules. In solids and in some colloidal solutions, where structures are built up through association forces, the physical and mechanical molecules may be quite different. When the units become very large, as in a macroscopic crystal or piece of a gel, the concept of the physical molecule becomes relatively unimportant, since the kinetic energy of translation acquired from thermal vibrations by a large particle plays only a small part in determining its properties. However, the larger the size of the units which hold together under a shearing force, the more important they are in determining the mechanical properties of a system. It is possible that in some cases the difference between the physical and mechanical molecule in a solid is merely a difference in point of view, but in other cases there seems to be a clear-cut physical distinction. In thixotropic systems such as vanadium pentoxide gels for example, the physical molecules of vanadium pentoxide may contain very large numbers of V_2O_5 particles. At very small shearing stresses the mechanical molecules may also be large groups of V_2O_5 particles, but at large shearing stresses the mechanical molecules may be the single V_2O_5 particles or micelles. The single water molecules, H_2O , as well as the polymers and perhaps the cybotactic groups¹¹ $(H_2O)_n$ are also mechanical molecules, the proportions of the different groups perhaps varying with temperature, rate of shear, etc.

The size of the mechanical molecule thus is not an invariant, as it changes not only with temperature, rate of shear, etc., but also, particularly in thixo-

¹¹ Stewart: *Rev. Modern Phys.*, 2, 116 (1930).

tropic systems, with the time of standing at rest. This is a part of the strength as well as the weakness of the concept; for, since it applies to a unit which can vary as conditions change, its use is not limited to infinitely dilute solutions or gases. The concept applies, for example, to gelatine or rubber solutions or from the most dilute (where the units of the solute which hold together during shear may be chemical molecules) to concentrated gels where association, thixotropy, etc., play important parts; it also applies to solids where the units held together by secondary forces may be more important than those held together by the primary valence forces.

The use of the concept of mechanical molecules makes it possible to avoid, for the time being, the problem of distinguishing between chemical molecules and micelles in dilute solutions, since from the standpoint of the mechanics of flow such a distinction is unnecessary. Likewise, the use of this concept clarifies other problems concerning the structure of solids, such as the question, "Is vulcanization a chemical or physical reaction?", by pointing out that it is the structure of the mechanical units which is important, whether these units are formed by physical or chemical means. It should be emphasized that our concepts are bound up with our methods of measurement and the concepts have value only when they are useful. In this paper the term molecule will be understood to be the mechanical molecule, except when it is specifically stated otherwise, since in most cases the chief interest is in the mechanical properties of the systems.

Ultimately there will probably be a quantum mechanics theory of molecular structure^{12,13,14} which will make the above divisions obsolete. However, until then, when these limited concepts must be used, there should be an awareness of their defects as well as of their advantages.

The Structure of Elastic Colloids

The outstanding properties which must be explained by any satisfactory theory of the structure of elastic colloids are:

1. High elasticity—*i.e.*, large deformations which are followed by recovery to substantially the original size and shape upon removal of the deforming force.
2. Storing up free energy on deformation and the return of a large part of it as external work during the recovery.
3. Hysteresis.
4. Elastic after-effect, or slow recovery long (even days) after the deforming force is removed.
5. Swelling in suitable liquids, and sometimes dissolving to give solutions of high viscosity.

In addition, the theory should not be inconsistent with such specific properties as the Joule heat, X-ray fiber diagrams, etc. It should also account for the fact that many gels are elastic, though not all elastic bodies are gels.

¹² Heitler: *Z. Physik*, **31**, 185 (1930).

¹³ Mulliken: *Chem. Rev.*, **9**, 347 (1931); *Rev. Modern Phys.*, **4**, 1 (1932).

¹⁴ Pauling: *Chem. Rev.*, **5**, 173 (1928).

The fact that elastic colloids can be deformed several hundred percent and then recover to their original shape implies the existence of structural units in the material which also have this property. The unit cannot be the atom, for work on the strength of crystals¹⁵ and metals,¹⁶ on band spectra,¹⁸ and on the Raman effect¹⁷ has shown that a very great force is required to increase the distance between adjacent atoms in a molecule or crystal by as much as 30%, and rupture or plastic flow occurs at relatively low elongations. To make possible the elongations observed in elastic colloids, it is essential, then, to have some unit of mechanical structure made of groups of atoms to magnify the limited deformability of the single atoms. Many such structures have been proposed, but in most cases the authors have suggested molecular arrangements which are not common to all elastic colloids (helical rubber molecules, for example) or they have not clearly recognized the essential factors required to produce elastic structures (two-phase gel theories). An analysis of deformation processes indicates that the property of high elasticity requires, and is produced by, the following factors:

1. Groups of atoms which form strong, somewhat flexible fibrous units. These mechanical molecules may be physical or chemical molecules as well.
2. Weak or uniform cohesive (secondary valence) forces around the fibers.
3. An interlocking of the fibers at a few places along their length to form a three-dimensional network. This interlocking of the fibers may occur through chemical combination, by secondary valence forces, or by mechanical entanglements.

4. A means of storing up free energy in the fibers during deformation.

Evidence for the existence and importance of these conditions in elastic colloids will be given, and then it will be shown how these criteria of the necessary and sufficient conditions for high elasticity help to correlate and explain some of the specific physical properties of rubber.

1. *Long Fibers.* The existence of a fibrous brushwork structure in two-phase gels is generally recognized. Such an arrangement is necessary to account for the fact that gels may be obtained containing only a few tenths of a percent dry solid,¹⁸ and that the rate of diffusion of molecules or ions through a gel differs only slightly from that in a sol of the same concentration.²¹

Usher and co-workers^{19,20} found that during the gelation of a gamboge sol one could actually observe the particles line up into filaments which form a three-dimensional network, and they inferred that a similar structure existed in gels of cadmium sulfide and other lyophobic materials. They also found that the viscosity of gas black and starch suspensions varied with the pressure only when there was a flocculated structure that could easily be broken up by small shearing forces. By means of a non-uniform dark field illumination,

¹⁵ Joffé: "Physics of Crystals" (1928).

¹⁶ Mehl: J. Am. Chem. Soc., **52**, 534 (1930).

¹⁷ Andrews: Phys. Rev., (2) **35**, 662 (1930).

¹⁸ Holmes and Maxson: Colloid Symposium Monograph, **5**, 287 (1928).

¹⁹ Usher: Proc. Roy. Soc., **125A**, 143 (1929).

²⁰ McDowell and Usher: Proc. Roy. Soc., **131A**, 409 (1931).

²¹ Reference 9, p. 727.

Szegvari²² showed that the ultramicroscopic particles of V_2O_5 formed filament or needle shaped groups when the V_2O_5 sols set to a gel, and recent work on the dielectric constants of thixotropic systems indicates that the filament formation during gelation is due to the contact and adhesion of the solid particles to each other, rather than to any immobilizing of the surrounding liquid.²³

Even in lyophilic gels, much of the liquid is mechanically entrapped in the interstices of some open structure rather than being bound by a chemical solvation, for one liquid in a gel can often be replaced by another of markedly different chemical properties without greatly changing its physical properties. The water in a gelatine gel, for example, may be replaced by organic liquids, or in some cases even by air.^{24,25}

X-rays have shown that elastic materials which are not two-phase systems also contain fibrous units. Crude and vulcanized rubbers show an x-ray fiber diagram when stretched,²⁶ as do stretched dried gelatine²⁷ and synthetic linear high polymers, provided their molecular weights are great enough.^{3,4,28,29} Solutions of these materials have high viscosities and show streaming double refraction.³⁰ For reasons discussed below a swelling agent must be used with some of these compounds to obtain high elasticity at ordinary temperatures.

While some sort of a fibrous mechanical structure is essential for high elasticity, the shape, stiffness, kinkiness, etc., of the fibers may vary widely among different systems. Nothing very definite is known about the precise shape of the fibers, other than that in materials like rubber, metastyrene, etc., the fibers are relatively thin and flexible—perhaps being only a single chemical molecule thick at most places—while in a fresh silica gel or a gamboge gel the fibers probably are many molecules thick and relatively stiff.

Purely geometrical considerations show, however, that the molecules of rubber do not have a helical shape, as has recently been proposed.^{31,32} If the fibers are twisted so that consecutive double bonds are adjacent to each other across one turn of the helix the maximum elongation possible is about 300% or only about one-fourth that actually found in rubber. To make possible the observed elongations, they would have to be in the form of helixes containing 16 atoms of 4 double bonds to a turn. Such a shape would not be stable, however, due to the tendency of large ring compounds to assume irregular forms and to flatten out so that the opposite sides of the ring are adjacent to each other.³³

²² Szegvari: *Z. Physik*, **21**, 348 (1924).

²³ Kistler: *J. Phys. Chem.*, **35**, 815 (1931); Kallman and Kreidl: *Z. physik. Chem.*, **A 159**, 322 (1932).

²⁴ Kistler: *J. Phys. Chem.*, **36**, 52 (1932).

²⁵ Erbring: *Kolloid-Z.*, **57**, 195 (1931).

²⁶ Meyer and Mark: *Ber.*, **61**, 1939 (1928).

²⁷ Katz and Gerngross: *Naturwissenschaften*, **13**, 900 (1925); Gerngross and Katz: *Kolloid-Z.*, **39**, 181 (1926).

²⁸ Carothers, Williams, Collins, and Kirby: *J. Am. Chem. Soc.*, **53**, 4203 (1931).

²⁹ Carothers and Hill: *J. Am. Chem. Soc.*, **54**, 1566, 1579 (1932).

³⁰ Signer: *Z. physik. Chem.*, **A150**, 257 (1930).

³¹ Kirchof: *Kautschuk*, **6**, 31 (1930).

³² Fikentscher and Mark: *Kautschuk*, **6**, 2 (1930).

³³ Reference 3, p. 378.

Staudinger's assumption that in dilute solution the molecules of linear high polymers are practically straight stiff elastic fibers does not seem reasonable in view of the possibility of rotation around single valence bonds, and this assumption is not necessary to explain his viscosity results. The most plausible hypothesis of the form of the rubber molecules in solution is that they are kinky fibers having a considerable range of lengths which mechanically entrap and practically immobilize a large volume of solvent.³⁴ This hypothesis is consistent with viscosity experiments carried on in this laboratory,³⁵ and with the collision areas of straight chain hydrocarbons calculated from the viscosity of their vapors.³⁶

2. *Weak Cohesive or Secondary Valence Forces.* Long fibrous units alone are not enough to produce elasticity. Parts of the fibers must be able to slide past each other without great difficulty if there are to be large deformations and recoveries. This implies weak or very uniform secondary valence forces around the greater part of each fiber, as well as implying a flexibility in the fibers themselves.

The weak secondary valence forces may be due to the arrangement of the atoms and so may be a property inherent in the fibers themselves, as is probably the case in rubber. In other cases the fibers have relatively strong cohesive forces, but these can be effectively weakened or insulated by combining the fibers with small molecules which have much weaker secondary valence forces—in other words by swelling the fibrous material with a liquid having a low viscosity. Numerous examples of producing elasticity by this method are known—swelling gelatine with water or glycerine, cellulose esters with dibutylphthalate, metastyrene with styrene, etc. In fact, this method of producing elasticity is so common that it has sometimes incorrectly been assumed that a two-phase gel structure was necessary for high elasticity.³ It is not two phases that are necessary, however, but rather forces of two different orders of magnitude, strong forces along the fiber and weak forces around the fiber.

Another way of reducing the magnitude of the secondary valence forces is to increase the distance between the molecules by raising the temperature. Metastyrene and rubber hydrochloride are made elastic by this treatment, and cured rubber loses its elasticity when cooled to sufficiently low temperatures.⁵⁷ Moreover, Bridgman found that rubber lost its elasticity and was very hard under extreme pressures.

Whitby⁴ recognized the importance of weak secondary valence forces when he attributed the slow recovery and what he called "the sub-permanent set" of elastic colloids to a high internal viscosity or an "elastic yield value." However, he states that the cohesive forces responsible for this "elastic yield value" are essentially the same as those responsible for the recovery of the materials after deformation, a view which does not entirely agree with that presented here. Von Weimarn⁷ also pointed out that non-uniform "vectorial

³⁴ Haller: *Kolloid-Z.*, **56**, 17 (1931).

³⁵ Busse and Karrer: "The Application of Dunn's Viscosity Equation to Rubber Solutions," Atlantic City Meeting of the American Chemical Society, September (1929).

³⁶ Melavan and Mack: *J. Am. Chem. Soc.*, **54**, 888 (1932).

force fields" around molecules made it possible to bring them into a rubbery state, but he also assumed that a helical structure was necessary for elasticity.

3. *An Interlocking of the Fibers at a Few Places along their Length.* The high deformability of elastic bodies is not unique, for liquids and plastics are easily deformed. It is the high recovery of elastic colloids which puts them in a class apart. Shearing stresses can distort and orient long molecules in liquids as well as in solids, as shown by the phenomena of streaming double refraction,³⁰ etc. However, when the shearing stress is relieved in liquids the molecules quickly slide past each other and assume a random orientation without changing the external shape. In elastic solids the return of the fibers to their normal kinky forms makes the whole sample return to its original shape, showing that there is an interlocking and binding of the fibrous units at a few places along their length which prevents their slipping completely past each other.

The effective strength of the bonds holding the fibers together may vary within wide limits, consequently the range of conditions under which a sample will be elastic, (*i.e.*, will recover almost completely) will be very different for different materials. Some bonds may be weak enough to be broken by relatively small shearing forces as in the thixotropic ferric oxide sols studied by Schalek and Szegvari,³⁷ the weak gels formed in ammonium oleate solutions, or the flocculated gas black and starch suspensions studied by Usher.²⁰ In these cases the structure broken by the shearing stresses may again be re-formed on standing. Probably the forces which produce a thixotropic structure are similar to those causing the flocculation of pigments and the formation of crystals.³⁹

In other cases the bonds between the fibers are stronger, formed, perhaps, by a mechanical entangling of the fibers, aided by the weak cohesive forces around the fibers. The structure of crude rubber and metastyrene is probably of this type. As one would expect, raising the temperature increases the ease of untangling the fibers, and these materials, therefore, show more slippage, or permanent set, at high temperatures.³⁸ Reducing the length of the fibers also reduces the chances of the fibers' tangling, and it is found that milling crude rubber, which probably shortens the fibers by an oxidation process^{40,41} greatly increases the flow or permanent set when it is subjected to a given force. While unvulcanized, dead-milled rubber flows readily under small forces applied for comparatively long times, it is nearly as elastic as cured rubber if the distorting force is applied for only a short time,⁴² *i.e.*, if there is not sufficient time for the thermal vibrations to aid in untangling the molecules.

In vulcanized soft rubber there are much stronger bonds holding the fibers together so that flow and permanent set are small at room temperature, though

³⁷ Kolloid-Z., 32, 318 (1923).

³⁸ Dieterich: Ind. Eng. Chem., 21, 768 (1929).

³⁹ Jong: Kolloidchem.-Beihefte, 29, 454 (1929).

⁴⁰ Cotton: Trans. Inst. Rubber Ind., 6, 487 (1931).

⁴¹ Busse: Ind. Eng. Chem., 24, 140 (1932).

⁴² Williams: Ind. Eng. Chem., 21, 872 (1929).

they become appreciable at high temperatures or over long times.⁴³ This suggests that vulcanization involves a chemical union between different rubber molecules, either through direct carbon to carbon bonds, or by means of sulfur (or Se, O₂, etc.) bridges.

The number of these bonds that exist in soft vulcanized rubber cannot be determined exactly, but some idea may be obtained of the upper and lower limits. The fact that vulcanized rubber can be elongated about 1000 percent of its original length indicates that in this system the interlocking of fibers cannot be more frequent on an average than about one bond for every ten carbon atoms of the chain. This is the upper limit for the number of bonds, and the actual number probably is far less than this. The work of Bruni and Oberto⁴⁴ indicates that a minimum of 0.15% sulfur or one atom for each 315 C₆H₅ radicals is necessary for vulcanization, *i.e.*, to produce a noticeable change in the mechanical properties of rubber. Assuming one bond for each sulfur atom, this represents one bond for every 1260 carbon atoms of the chain, which is the extreme lower limit for the number of bonds necessary to affect the stress-strain curve appreciably. If it is assumed that vulcanized rubber is a chemically distinct material, and that two bonds are required for each original chemical molecule, these results indicate a molecular weight of the order of 20,000 for the particular sample of crude rubber which they used. If the theory of elastic deformation presented here is correct, the minimum sulfur required for vulcanization should increase with the amount of mastication of the rubber. One would also expect the amount of combined sulfur required for maximum strength to increase with the amount of mastication and these are found to be the facts.

Blake⁴⁵ reports that only 5.2% Se can combine with rubber in the soft rubber cure. If we assume that each Se atom forms a bond between two fibers, there would be a maximum of about one bond for every 23 isoprene groups, or one bond for every 92 carbon atoms in the chain, which, from mechanical considerations, is a reasonable figure.

The necessity for interlocking of the fibers of a gel at a few places along their length was recognized by Kistler,²⁴ who found that a cellophane aero-gel could be made with a volume 100% greater than the original cellophane, yet with nearly the same strength as the original. In the case of systems made of very flexible fibers such as rubber or gelatine, he could not produce an aero-gel. However, on stiffening the fibers, as on tanning a gelatine gel with formaldehyde, which increased the stiffness of the gel presumably by tying different fibers together with strong bonds, he was able to obtain a gelatine-aero gel.

4. *A Means of storing up Energy during the Distortion of the Fibers.* Since elastic bodies can do work on retraction they must have a means of storing up free energy when they are distorted. This energy may in part be stored as potential energy in the fibers, because of a slight increase in the dis-

⁴³ Van Rossem and van der Meyden: *Rubber Age*, N. Y., **23**, 438 (1928).

⁴⁴ *Rev. gén. caoutchouc*, **8**, No. 75, 19 (1931).

⁴⁵ *Ind. Eng. Chem.*, **22**, 744 (1930).

tance between adjacent atoms in the fibers and through a distortion of the valence angles. This idea of a stiffness in the fibers is consistent with the concept of tetrahedral carbon atoms⁴⁶ and it also agrees with the new wave mechanics.^{47,48} It does not follow, however, that the fibers are even approximately straight rods, or that they have the zig-zag shape attributed to fatty acid molecules closely packed on the surface of water. In long molecules, the thermal vibrations instead of causing the molecules to vibrate as thin glass fibers might easily cause rotation around single valence bonds to produce a very kinky shape. Haller⁶ has calculated, on the basis of Raman spectra data for the energy required to deform valence angles, that if the molecules vibrated as rods, the average bending of a paraffin hydrocarbon chain of 100 carbon atoms would be an angle of about 16.4° , while a chain of 10,000 carbon atoms would be bent, on the average, 163.5° from a straight line. It follows from purely geometrical reasons that thermal vibrations will have a strong tendency to restore a kinky shape to long fibrous molecules after they have been straightened by an external force.⁴⁹ Probably at all times there will be a rapid interchange of potential and kinetic energy due to thermal vibrations.

When the fibers are in nearly parallel alignment the effect of thermal vibration in causing contraction may be more than counterbalanced by the tendency of the molecules to form crystalline units with evolution of heat. This is exhibited as racking and as the Joule heat in rubber, and similar effects are observed in chloroprene.²⁸ Such an effect can be expected only when there is a uniform periodicity in the intensity of the secondary valence forces such as would be obtained when the fibers are made by repeating some simple unit.

If the recovery of elastic colloids is due to the potential energy stored in the distorted atoms and to the effect of thermal vibrations, the elasticity of chemically saturated materials such as gelatine, metastyrene, etc., and of unsaturated ones such as rubber, may be explained on the same basis. It is not necessary then to account for the elasticity of rubber on the basis of the attraction of double bonds across the turns of the helix.^{26,50} Nor is this helical structure necessary to account for the S-shape of the stress-strain curve of rubber; for if the stress-strain curve of rubber is calculated on the basis of the instantaneous cross sections of the sample, it is not S-shaped.^{51,52}

This stiffness of the fibers also accounts for the swelling pressure of gels. If the fibers are in the normal random kinky shape when a gel such as gelatine is formed in solution, the fibers on drying will be distorted as the gel contracts in size because of the capillary and cohesive forces. After the liquid is evaporated, the cohesion between the separate fibers is great enough to keep them in their distorted positions, in spite of the thermal vibrations which tend to relieve strains at the valence angles. On again putting the gel in water,

⁴⁶ Kettering, Shutts, and Andrews: *Phys. Rev.*, (2) **36**, 531 (1930).

⁴⁷ Slater: *Phys. Rev.*, (2) **37**, 481 (1931).

⁴⁸ Pauling: *J. Am. Chem. Soc.*, **54**, 988 (1932).

⁴⁹ Karrer: *Phys. Rev.*, (2) **39**, 857 (1932).

⁵⁰ Fikentscher and Mark: *Kolloid-Z.*, **49**, 135 (1929).

⁵¹ Hatschek: *J. Soc. Chem. Ind.*, **40**, 251 T (1921).

⁵² Ariano: *India Rubber J.*, **72**, 271 (1926).

the cohesive (or secondary valence) forces around the molecules will be satisfied by the smaller water molecules, and the fibers can then untangle so as to relieve the distortion as much as possible.

The swelling of a gel, then, consists of two parts. The first is an adsorption of the swelling liquid on the gel fibers by means of the secondary valence forces which may involve a liberation of heat. The adsorbed layer effectively insulates these secondary valence forces, thus allowing the fibers to move past each other and assume a random kinky shape with the minimum average distortion of the valence angles. This latter part of the expansion may involve an absorption of heat, even though there is a decrease in free energy.

As the swelling continues new positions of strain may be introduced into the molecules and these may finally balance any further tendency to swell. This limited swelling occurs only when the molecules are long enough to be quite firmly tangled or snarled, or when there is a combination of molecules through very strong forces (polymerization, etc.) to make the sample a mechanical unit, as probably is the case in cured rubber. This effect also appears in gelatine gels which have been formed from solutions of different concentrations. The amount of water they will again take up after drying will be found to depend on the concentration at which the gel was formed, the gels formed from dilute sols taking up more water than gels from concentrated sols.⁵³ The contacts made at the time the gel is formed determine the amount of swelling that will produce the minimum distortion of the valence angles. The anisotropic swelling of gelatine gels observed by Sheppard and McNally⁵⁴ also shows that there are strains in the dry gels determined by the conditions under which the gels are formed and dried.

This theory of the cause of the swelling pressure gives a very simple explanation of the results of Stamberger and Blow,⁵⁵ who found that a given concentration crude rubber produced the same swelling pressure as dead-milled rubber, though one was a swollen gel and the other a relatively mobile liquid. The effect produced by the tangled molecules trying to expand and minimize the distortion of the valence angles may be visualized as being somewhat similar to the effect produced when a number of tennis balls is placed in a cylinder and compressed by a piston. The balls will exert a given pressure when compressed a definite amount by the piston, and on removing the piston the balls can be poured out of the cylinder. If, however, the balls are coated with an adhesive and then packed into the cylinder in the same way and the adhesive allowed to dry, the balls will be fastened together wherever they come into contact in their undeformed state. The balls will exert the same pressure as before when compressed by the piston, and on removing the piston the group of balls will regain its original shape, but the individual balls cannot be poured out of the cylinder. Similar results would be obtained if the molecules were considered as tangled springs instead of tennis balls. If this picture is correct, and the swelling pressure is independent of molecular size, it

⁵³ Reference 9, p. 209.

⁵⁴ Sheppard and McNally: *Colloid Symposium Monograph*, 7, 17 (1929).

⁵⁵ Stamberger and Blow: *Kautschuk*, 6, 22 (1930).

follows that in concentrated solutions, where swelling pressures can be measured, and for compressive stresses, such as are applied in measuring swelling pressures, the volume occupied by the mechanical molecules is proportional to their weight. This relation is very different from the results found by Staudinger¹ and Fikentscher and Mark⁵⁰ for dilute solutions, but it is consistent with the view that in solids and concentrated gels the molecules have a more or less compact kinky shape.

Since this paper was presented, a paper by Meyer, von Susich and Valko⁷⁰ has appeared in which they abandon the idea of a helical rubber molecule, and conclude that one must avoid the use of models if he is to get a fundamental understanding of the mechanism of elastic deformation. The kinetic theory of elasticity which they present emphasizes the factor of thermal vibrations of groups of atoms within the molecule, and is consistent with the theory given above.

Application of Theory to Specific Properties of Rubber

This theory is of value in interpreting and correlating many of the specific physical properties of elastic systems. In the case of rubber, for example, the theory does not tell anything about the proper accelerators of vulcanization to be used to produce definite properties such as low permanent set, or low hysteresis, or high elongations. However, accepting the view that crude rubber consists of long, kinky, fibrous molecules, and that soft rubber vulcanization produces strong (presumably chemical) bonds between the molecules of crude rubber, one would expect, and actually finds, the following physical properties accompanying those already considered.

1. *Creep and Elastic After-Effect.* Even with relatively weak cohesive forces around the fibers one would expect that any large elongation or recovery would cause the kinky fibers to move so far that some parts would become jammed or tangled up in intermediate equilibrium positions. The energy of thermal vibrations would then cause the jammed groups of atoms, or parts of fibers, to escape slowly from these temporary equilibrium positions and become at least partly untangled. This produces a slow creep after the initial rapid elongation, when the sample is stretched by a constant load. If the rubber is stretched to a constant elongation, this untangling will be manifested as a slow decrease in the stress.

When a stretched sample of rubber retracts, groups of atoms again have to move considerable distances past other rubber molecules, and there is as much chance of these groups jamming in intermediate equilibrium positions as there was during the stretching. These tangles are undone only when the energies of the thermal vibration are great enough to move the groups out of the intermediate equilibrium positions. The resultant continued retraction is the elastic after-effect.

A mathematical treatment of this process is very difficult, and only by making some rather improbable assumptions was it possible to derive rela-

⁷⁰ Meyer, von Susich and Valko: *Kolloid-Z.*, **59**, 208 (1932).

tions between length and time which approximately fit the experimental results. Phillips,⁵⁶ found that the increase in the length on stretching for vulcanized rubber was given by the formula

$$E = a + b \log t$$

where E is the increase in length, t is the time, a and b are constants. For unvulcanized rubber the formula was of the type

$$\log E = a + b \log t$$

Work in this laboratory has indicated that the latter formula is valid for certain kinds of vulcanized rubber, also.

This explanation of the elastic after-effect, of course, is analogous to the explanation of the slowness of many chemical reactions. A knowledge of the temperature coefficient of this process (measured without complicating side effects) would permit the calculation of the average amount of energy that must be added to a molecule or part of a molecule to remove it from these intermediate equilibrium configurations, or jams, just as a knowledge of the temperature coefficients of chemical reactions makes it possible to calculate the heats of activation.

Elastic after-effects may be produced by the tendency to form fibrous crystals, as well as by the mechanical jamming of the fibers. The racking of crude rubber is an extreme example of this effect. Here the slowness of the retraction is due to time required for the sample to acquire from the outside the heat necessary to melt the crystals, so it might be called a thermal elastic after-effect. Both types of elastic after-effects are reduced by raising the temperature. On lowering the temperature there should be more tangling of the fibers and the rate of disentangling should decrease, due to the greater magnitude of the cohesive forces around the fibers, causing the modulus of rubber to increase as the temperature is lowered, as was found by Mark and Valko⁵⁷ and by Rosbaud and Schmid.⁵⁸

It may be mentioned that no elastic after-effect other than that due to thermal, electrical or other secondary thermodynamic effects can occur in a perfect crystal.⁵⁹ An elastic after-effect produced by shearing forces requires the existence within the sample of groups of atoms held together by strong forces and surrounded by weak forces.

The mechanism of the jamming of large groups of atoms during deformation and recovery suggested above leads one to expect that rubber will exhibit a higher modulus,—that is, a lower elongation for a given force,—if the force is applied quickly rather than slowly; this actually occurs. Further evidence for the jamming and tangling of the molecules on distortion is found in the experiments of Prache.⁶⁰ On loading a sample of crude rubber with a 400-

⁵⁶ Phys. Soc. London, January 29 (1905).

⁵⁷ Rev. gén. caoutchouc, 7, No. 64, 11 (1930).

⁵⁸ Z. tech. Physik, 9, 98 (1928).

⁵⁹ Reference 15, p. 23.

⁶⁰ "Le Caoutchouc and Gutta Percha," 15003 (1930).

gram weight he obtained a certain elongation. On reducing the weight to 100 grams the sample contracted to a length less than it would have had if this 100-gram weight had been applied originally. After this contraction the sample then slowly stretched to its normal length under a 100-gram load. The stretching under the 400-gram weight evidently was more rapid than it would have been with a 100-gram load, so there was more jamming of groups in intermediate positions, making the sample stiffer, and causing a larger contraction upon removal of the weight. Rearrangement and untangling of these jammed groups then permitted the sample to further elongate to its normal length when stretched by a 100-gram weight. A similar result was obtained by Mr. Davies of this laboratory by compressing samples of uncured rubber under different weights in the Goodrich plastometer.⁶¹

3. *Permanent Set.* If the sample does not completely recover from a deformation it is said to have acquired a set. It is important to distinguish between two very different conditions which may produce this effect. The first is a true permanent set, produced when the fibrous molecules are not firmly interlocked. In this case the molecules may relax by sliding completely past each other. This is simply a viscous or plastic flow which reduces the strain in the molecule without changing the external shape of the sample. If this action is carried to the limit the sample becomes isotropic. Anything which will decrease the binding between the fibers, such as raising the temperature, swelling with solvents, etc., will increase the permanent set produced by this cause; reducing the length of the molecules will have the same effect. Milled rubber acquires a greater permanent set than unmilled rubber and the permanent set is lowest for the highest members of a homologous series of polymers.

The second cause of permanent set is essentially a very slow elastic after-effect, usually a thermal elastic after-effect as in racked crude rubber. If the temperature is lowered far enough, cured rubber will show a similar effect, for at the lower temperature the balance between the cohesive forces, thermal vibrations and strains at the valence angles is changed so the molecules no longer can contract. Whitby called this slow elastic after-effect the "sub-permanent set." Raising the temperature or adding solvents to rubber will reduce this type of elastic after-effect.

It follows from this mechanism that not only will the modulus of the rubber increase, but the permanent set will decrease when the speed of deformation increases. The elastic recovery of crude milled rubber is nearly as great as that of cured rubber if the time of deformation is small. This can be demonstrated by bouncing balls made of cured rubber and milled crude rubber. They will bounce to nearly the same height, although they have very different values for stiffness and permanent set when the loads are applied for longer times.⁴² In a rapid deformation cycle the mechanical tangling and jamming of the molecules is sufficient to keep them from flowing even though there are no strong chemical bonds holding the fibers together. There is not enough time for thermal vibration to aid in getting the molecules out of the intermediate equilibrium positions or to flow. The sample, therefore, shows a high recovery.

⁶¹ Karrer, Davies and Dieterich: Ind. Eng. Chem., Anal. Ed., 2, 96 (1930):

4. *Hysteresis.* For a minimum hysteresis in a sample of rubber which is subjected to mechanical distortion, it is necessary to reduce to a minimum the slow creep and elastic after-effects as well as the plastic flow. Such a result would be accomplished if there were a weak binding force or attraction between the molecules permitting them to slide past one another easily everywhere except at the few points where there is the strong interlocking necessary to prevent plastic flow. This condition may be realized if rubber is swollen with a large amount of oil and then vulcanized. The quivering of a cured cement, for example, shows that its hysteresis actually is very low, at least for small deformations.

The hysteresis due to the tangling and untangling of the molecules may be reduced by going through the deformation cycle either very rapidly or very slowly, provided the permanent set is low. In the first case there will be a great deal of tangling. However, since there is little time for the fibers to become untangled the sample will exert nearly the same force during the recovery as it does during the stretching. In the second case, when the rate of stretching and recovery is very slow the thermal vibrations enable the fibers to take up equilibrium positions during both the stretching and recovery, so the hysteresis loop is small if there is no permanent set.

Another method of reducing hysteresis and securing equilibrium stress-strain curves is to help the molecules out of the jams by making the sample oscillate during the stretching. Stress-strain curves of this type were obtained by Gerke.⁶² One would expect from thermodynamic considerations that the modulus of the rubber would be somewhat greater at high temperature than at low temperature for the stress-strain curves obtained in this way, and the limited data reported by Gerke indicated that such may be the case. His results also showed that time of cure has no effect on the equilibrium stress-strain curve and he cited this as evidence that the curing of rubber affects the plastic properties of rubber more than the elastic properties; Williams⁶² reached a similar conclusion from the study of stress-strain curves at high speeds. It is evident that cure influences the elastic after-effect and creep as well as the plastic flow, and these are parts of the elastic properties of rubber.

This analysis of the deformation of rubber differs considerably from that of Ariano⁶³ who postulated a "point of viscous diffusion," "plastic state," and "liquid viscous state" between the solid and liquid states to explain the observed elastic properties. As a real explanation of the behavior of rubber under mechanical distortion, the molecular mechanism suggested above seems greatly preferable to naming hypothetical states between idealized solid and liquid states.

5. *Other Physical Properties.* The optical properties sometimes give considerable information about the chemical as well as the physical structure of materials. Recent work on the Raman spectra provides a very convenient method for studying the infra-red absorption spectra of various materials, and it was thought that this line of attack might show something about the struc-

⁶² Ind. Eng. Chem., 22, 73 (1930).

⁶³ Nuovo Cimento, March 1929; India Rubber J., 78, 316 (1929).

ture of rubber and similar hydrocarbons. Preliminary experiments were carried out by Professor Williams and Mr. Hollaender at the University of Wisconsin, to see if the Raman spectra of rubber, gutta-percha and balata in carbon tetrachloride solutions showed any distinctive differences. Since the materials were all carefully purified they darkened readily through oxidation on exposure to air. This made it difficult to obtain the Raman spectra. On exposure to a mercury arc, however, the gutta-percha solution showed a few Raman lines around 4600 \AA , probably excited by the mercury line 4359 \AA , and a broad band around 4780 \AA . Pale crepe and balata showed similar bands. Others have also found broad bands in studying the Raman effect of rubber solutions.⁶⁴ The fact that bands rather than lines are obtained may be due to the high viscosity of the solution, or it may indicate that the rubber groups can respond to a wide range of frequencies. It was found in this work that all the solutions gelled on the side exposed to the light, although they were in pyrex glass vessels which transmit only down to a wave-length of 3200 \AA . This gel structure formed in gutta-percha and balata as well as in rubber. It probably is not identical with that produced by vulcanization with sulfur or sulfur chloride, but at least it involves the linking together, by rather strong bonds, of units which previously were separated.

The tendency of kinky fiber molecules to expand and relieve the internal stresses accounts for the swelling pressure and the mechanical entrapping of liquids by gels, and it also implies that a similar mechanical entrapping of solvent should occur in solutions. Work done in this laboratory³⁵ several years ago on the temperature coefficient of the viscosity of rubber solutions supports the view that their high viscosity is due to this cause.

Dunn,⁶⁵ Andrade⁶⁶ and others have shown that the change of viscosity with temperature of non-associated liquids can be represented by an equation of the type $\log 1/\eta = A/T + B$, where η is the viscosity, T the absolute temperature, and A and B are constants. By assuming that the fluidity ($1/\eta$) is a measure of the rate at which molecules acquire sufficient energy q to leave their transient equilibrium positions (cybotactic state⁶⁷), the writer derived the above relation between fluidity and temperature in the form $1/\eta = CS^{r-1} e^{-q/kT}$, where S is the shearing stress, C and r are constants, and the other terms have their usual significance. This equation includes the relation between shear and fluidity found by Nutting. The validity of this interpretation of viscosity is confirmed by data recently published showing the relation of viscosity to the perfection of orientation for 22 octyl alcohols.⁶⁷ The changes in the constants C and q , or A and B can, therefore, be interpreted in terms of changes in the structure of the solutions. Tests on rubber solutions in several solvents and over a wide range of temperature and concentrations showed that the value of q in pure solvents differed only slightly from the values in rubber solutions, provided they were not too concentrated.

⁶⁴ Franklin and Laird: *Phys. Rev.*, (2) 36, 147 (1930).

⁶⁵ *Trans. Faraday Soc.*, 22, 401 (1926).

⁶⁶ *Nature*, 125, 582 (1930).

⁶⁷ Stewart and Edwards: *Phys. Rev.*, (2) 38, 1575 (1931).

If there were an adsorptive binding of the solvent to the rubber molecules such as was assumed by Fikentscher and Mark,⁵⁰ one would not expect this result, so it is probable that the binding of the solvent molecules is largely a mechanical entangling.

6. *Cured Racked Rubber.* Fibrous rubber has been produced in various ways: racked rubber which has been cooled to liquid air temperatures can be shattered to show a fibrous structure; Kirchhof⁶⁸ and Mark and Susich⁶⁹ obtained fibrous materials by allowing racked rubber to react with sulfuric acid, chlorine, bromine, and iodine at low temperatures for periods up to several months. Mechanically fibrous materials were obtained in every case, but the bromine treated rubber did not give an x-ray fiber diagram. All these materials were relatively weak or brittle and did not have any remarkable physical properties.

From the above theory of rubber structure it was thought that vulcanizing rubber destroys its ability to become racked for one of two reasons. If during vulcanization random bonds are introduced between the fibers this will cause additional strains and distortions when the fibers are arranged parallel to one another by an external force, and the additional strains will prevent the secondary valence forces from holding the fibers in position except at very low temperatures. It is also possible that the chemical reaction during cure changes the intensity and distribution of the secondary valence forces so that the fibers cannot be made parallel, or else the forces are not strong enough to hold them parallel if they are oriented by an external force. In either case one would expect to obtain a rather interesting product if the rubber were first racked and then cured. Attempts to cure racked rubber with sulfur and ultra accelerators at room temperature or slightly above usually resulted in producing what was in effect merely a cured rubber with a strong calender grain.

When racked rubber was cured in a stream of dry sulfur chloride vapor, a strong, horny, fibrous product was obtained with rather unusual properties. It was found that the tensile strength of the samples depended greatly upon the elongation previous to cure, just as the strength of rubber at very low temperatures depends on the elongation of the sample before cooling.⁵⁷ In one case sheets of evaporated latex 0.005" thick were cured in a stream of dry sulfur chloride vapor for 15 min. at 0°C, after being racked different amounts. The tensile strengths varied from about 200 to 17,000 lbs./sq. in., as shown in the following table:

Initial Stretch	Tensile Properties of Cured Sample	
	Ultimate Elongation	Tensile Strength
0%	15%	220 lbs./sq. in.
300	20	4,560
600	20	7,070
900	30	10,450
1200	25	17,100

⁶⁸ Kautschuk, 5, 9 (1929).

⁶⁹ Kolloid-Z., 46, 11 (1928).

Similar results have been obtained at room temperature or even higher, over a wide range of curing times. If the samples are very thick only the surface is cured leaving the inside still uncured even after several hours, and the samples are relatively weak and brittle. It is probable that the tensile strengths shown in the above table are not the maximum that can be produced, and it is likely that rubber fibers can be prepared with a strength comparable to the best textile fibers. Samples of cured racked rubber gave sharp x-ray fiber diagrams.

The fibrous product is cured to the hard rubber stage by the sulfur chloride. In one case a 30-minute cure gave a material containing 15.2% sulfur, while the compound $(C_{10}H_{16})_2 S_2Cl_2$ requires 15.7% sulfur. The cured racked rubber may be left in sulfur chloride vapor up to 15 hours without noticeably changing its tensile properties, although the unstretched rubber becomes very brittle when left in the vapor for fifteen minutes.

From the point of view of the mechanical structure of rubber presented here one would expect that fibers could be obtained by stretching cured soft rubber and further curing it in sulfur chloride vapor while stretched. This was tried, using a rubber-sulfur mixture and accelerated stocks, and fibrous rubbers were obtained in every case. However, the accelerators, zinc oxide, age resisters and other compounding ingredients made it necessary to increase the time of cure, and the final product was not quite as good as that obtained with crude unmilled rubber. This may have been because the cured rubber could not be elongated as much as the evaporated latex.

If the rubber is stretched in two directions at once and then cured, a very interesting non-fibrous parchment-like material is obtained. In this case the molecules probably are stretched out into fibers which are oriented at random in a plane. The product is quite strong and flexible in thin sheets, and is very resistant to organic liquids, even boiling toluene does not change it appreciably.

Summary

1. Some of the concepts included in the term "molecule" are briefly discussed and it is pointed out that the mechanical molecule is often the most important one in colloid systems.
2. The elastic properties of colloid systems require, and are produced by a group of four factors:
 - (a) Long fibrous molecules.
 - (b) Weak or uniform cohesive forces around the fibers.
 - (c) An interlocking of the fibers.
 - (d) A means of storing up free energy when the fibers are distorted.
3. Evidence for the existence of these factors in elastic colloids is discussed and is applied to account for and correlate some of their physical properties.
4. The theory of the structure of elastic colloids presented here has suggested means of preparing fibrous and parchment-like rubbers having rather unusual properties.

*Physical Research Laboratory,
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May 10, 1932.*

THE SEPARATION AND IDENTIFICATION OF SOL RUBBER HYDROCARBONS

BY THOMAS MIDGLEY, JR. AND ALBERT L. HENNE

The hydrocarbon occurring in natural rubber is not homogeneous. This has been demonstrated repeatedly by separation into a more soluble portion, called "sol rubber," and a less soluble portion, called "gel rubber."

A variety of methods, all based on solubility difference, have been employed to bring the separation about. The best known are: (1) the slow diffusion of rubber in petroleum ether, a method originated by Caspari¹ and improved by Feuchter² and by Pummerer and Miedel,³ and (2) the separation by means of absolute ether into an "ether-soluble portion" and an "ether-insoluble portion."⁴ However, the same methods in the hands of different experimenters have given discordant results, and the conclusions have been debatable. For instance, Hauser⁵ found that after a first separation, rubber can be refractionated again into sol and gel rubber and from this he concludes that sol and gel form an equilibrium mixture which will automatically be regained when one of its constituents is decreased or eliminated. Whitby⁶ observes that different solvents furnish different ratios of sol/gel, and he concludes that the rubber hydrocarbon is a mixture of molecules of varied sizes.

It appears that the investigators employing diffusion methods, implicitly assumed that sol and gel rubber were not miscible in each other, and that in its essence, the separation was analogous to that of sugar from sand by water.

The apparently incoherent results obtained by diffusion separation are rendered quite reasonable when the mutual solubility of sol and gel is taken into account. A single diffusion of rubber in a given solvent establishes a two phase system, each phase of which contains both sol and gel rubbers, but in different proportions. In other words, diffusion accomplishes only a partial separation.

As a means of coarse separation, diffusion is quite acceptable; but if complete separation is desired, refractionation until the fractions are no longer altered is essential. For this purpose, diffusion is unsatisfactory, because the length of time required to reach equilibrium is sufficient to allow the rubber solution to degrade.

Proponents of the diffusion methods may argue that degradation occurs only in the presence of oxygen, and that a fractionation by repeated diffusion in an inert atmosphere cannot be criticized. This may be true. But it must be borne in mind that given sufficient time, minute quantities of oxygen are

¹ Caspari: *J. Soc. Chem. Ind.*, **32**, 1041 (1913).

² Feuchter: *Kolloidchem. Beihefte*, **20**, 434 (1925).

³ Pummerer and Miedel: *Ber.*, **60**, 2148 (1927).

⁴ Pummerer: *Kautschuk*, **1927**, 233-6; Pummerer and Pahl: *Ber.*, **60**, 2152-63 (1927).

⁵ Bary and Hauser: *Rev. gén. caoutchouc*, **1928**, No. 42, 3-11.

⁶ *Trans. Inst. Rubber Ind.*, **5**, 184-95 (1929); **6**, 40-62 (1930).

sufficient to cause considerable degradation, and the complete elimination of oxygen is a difficult experimental accomplishment. Hence, the diffusion method is not practical for refractionation.

A method of fractionation based on precipitation at different temperatures has been described and advocated in a series of previous papers.⁷ This method is not subject to the same criticism as the diffusion method, because it establishes equilibrium in a short period of time. The degradation which occurs despite the careful elimination of oxygen during the procedure is so slight that it does not obscure the results nor vitiate their interpretation.

Method of Separation

The temperature differential method is based on the different solubilities of the hydrocarbons of rubber in a certain solvent, at a certain temperature. It makes use of the fact that mixtures of rubber, benzene and alcohol are single-phased within certain limits of concentration and temperature, and, upon cooling, separate into two phases at a definite temperature. One of the phases contains the sol rubber in preponderant quantity, the other contains most of the gel rubber. By repeating the process the preponderant constituent of one of the phases is progressively freed of the principal constituent of the other phase. The experimental details and the efficiency of the procedure are outlined in the appendix.

Criterion of Identification

No fractional procedure of any kind can be satisfactorily performed without a criterion to judge the progress of the fractionation. The measurement of a physical constant such as density, refractive index, melting point, etc., is generally used: in the case of rubber, this is impractical, and consequently a specially standardized physical constant has been devised and called "standard precipitation point," or by abbreviation, "s.p.p."

The standard precipitation point is defined as the temperature at which a slowly cooled mixture of 0.85% of rubber, 28.55% absolute alcohol and 70.60% benzene shows a sudden increase of turbidity. The experimental details needed to measure an s.p.p. are given in the appendix.

Results

The application of the temperature fractionation method, controlled by adequate s.p.p. determinations to a variety of rubber specimens has given the results graphically represented in Figs. 1 to 4. The mode of representation is the same as for an Engler distillation.

In addition to the preceding cases, a sample of smoked sheet was fractionated: the s.p.p. of its sol fraction was found to be 34.8°.

Irrespective of their source, the sol rubbers present the same characteristics, *i.e.*, they are white, translucent, semi-plastic, elastic substances. Tackiness is absent from s.p.p. 33° upwards, but is quite noticeable at s.p.p. 32° or lower. Pure sol rubbers are unstable at room temperature. Degradation is detectable after a few days despite precautions against oxygen. Storage in

⁷ Midgley, Henne and Renoll: J. Am. Chem. Soc., 53, 2733 (1931); 54, 3343, 3381 (1932).

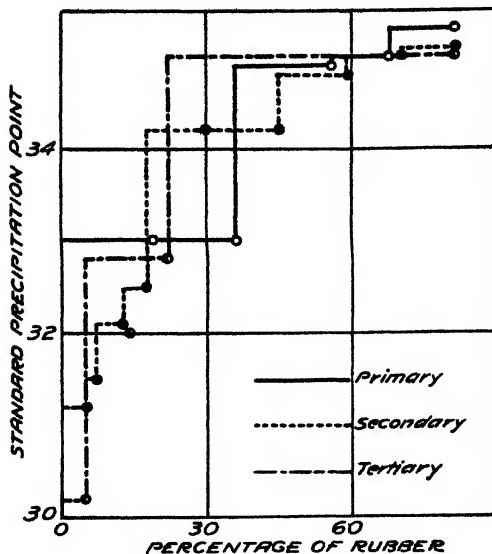


FIG. 1

Fractionation of Crepe Rubber

solid carbon dioxide retards degradation but does not prevent it completely. No tendency to form gel rubber, or equilibrium mixtures thereof has been observed.

Interpretation

A comparison of the results reported in Fig. 1 (pale crepe) and Fig. 2 (milled rubber) shows that extreme milling degrades both sol and gel rubbers. Hence it is reasonable to assume that the presence of components of low s.p.p. in Fig. 1, is due to the sheeting process undergone by the rubber before being

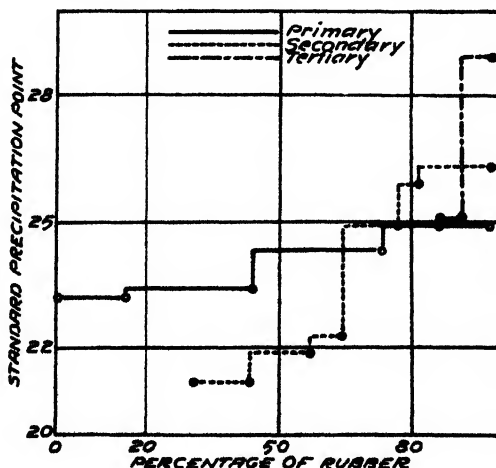


FIG. 2

Fractionation of Milled Rubber

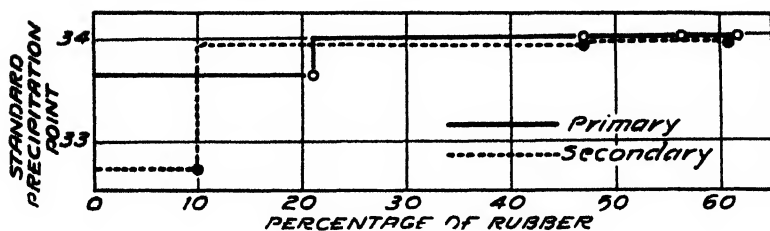


FIG. 3
Fractionation of Spray Rubber

baled. With this in mind, the results reported in Fig. 3 (sprayed rubber) indicate that nature produces only one sol rubber in a given specimen. This does not mean that natural sol rubber is a single invariable compound; variations occur between sol rubbers of different specimens. The limited number of specimens studied, and their insufficiently known history preclude, at the present time, any conclusion as to the factors involved in this variability. Seasonal, soil, and climatic conditions suggest themselves as suitable for continued research.

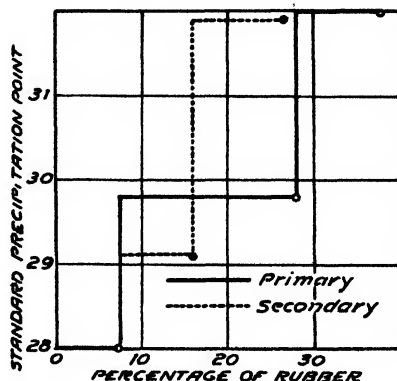


FIG. 4
Fractionation of Guayule Rubber

Conclusions

- (1) Nature produces a definite sol component in any single specimen of natural rubber.
- (2) The sol component can be separated and purified by refractionation methods.
- (3) Purified sol rubber retains the physical properties of natural rubber; it can be vulcanized to yield a product of superior qualities.
- (4) No experimental evidence exists to justify the opinion that rubber is a two-phase system.
- (5) Sol rubber and gel rubber are mutually soluble.

Appendix

Determination of the Standard Precipitation Point, s.p.p. A 1.288 g sample of the rubber (free from solvent) is placed in a 250 cc Erlenmeyer flask. One hundred cc of C.P. benzene is added. The flask is set away in the dark, under CO₂, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc of benzene and 56 cc of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees C is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experimental precipitation point. It is reproduc-

ible to $\pm 0.1^\circ$. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250 cc receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to insure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified CO_2 through the system, the solvents are distilled with a steam bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0° . From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1% . By means of the chart Fig. 2, paper VII,⁷ the experimental precipitation point is then corrected to standard conditions, viz. 28.55% alcohol and 0.85% rubber. This is the s.p.p.

Fractionation Procedure. Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% was dissolved in 8083 g of benzene, heated to about 50° . A hot mixture of 4500 cc of absolute alcohol and 1400 cc of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50 cc sample, was 43.0° . The mixture was then held at 42.0° in a thermostat, for one hour. At the end of this period, the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g of rubber hydrocarbon, hereafter designated as A_1 . After removal of the A_1 rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of 43.5° . Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g of rubber hydrocarbon was obtained, called A_2 hereafter. Two repetitions of these operations yielded fractions A_3 and A_4 .

After the fraction A_4 had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol-benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A_5 . Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A_6 , while the insoluble matter was called B.

Efficiency of the Procedure. The efficiency of the separation method is illustrated as follows. A 10 g specimen (s.p.p. 35°) and a 10 g specimen (s.p.p. 28.9°) were dissolved in the same batch of benzene and separated by fractional precipitation. A single fractionation yielded 11.5 g of (s.p.p. 34.9°) 8.5 g of (s.p.p. 28.5°).

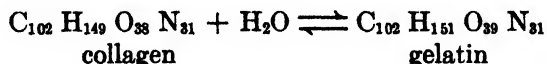
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THE STRUCTURE OF GELATIN SOLS AND GELS

Part V. The Insolubilization of Gelatin by Heat

BY S. E. SHEPPARD AND R. C. HOUCK*

Insolubilization of gelatin, *i.e.*, loss of capacity to dissolve completely in water at 40°C and above, appears to have been first observed by Hofmeister.¹ He found that gelatin which had been heated to 130°C was not readily soluble in water, in fact could only be brought into solution by boiling for several hours. Bogue² found that glue heated at 110°C for 15 hours became insoluble. The change was attributed by Hofmeister to a reversal of conversion of collagen to gelatin which he expressed by the equation



He regarded collagen as the anhydride of gelatin. There appears to be no definite evidence either for this particular molar ratio of collagen to water as essential for the transformation, nor for a molecular unit of the magnitude 2500 for collagen.

Emmett and Gies³ disputed Hofmeister's theory of reconversion. They claimed that heated gelatin was digested by trypsin, while collagen was not. They further stated that collagen loses ammonia on conversion to gelatin with boiling water, while the insolubilized gelatin gives up no ammonia on heating with water. This last statement appears to us to be generally incorrect; we have not found any evidence of ammonia being liberated in the conversion of hide collagen to gelatin—provided the collagen had been delimed and neutralized.

The Relation of Gelatin to Collagen

In the first paper of this series⁴ dealing with the viscosity of gelatin sols and its change on heating, the following theory of gelatin formation was proposed: "We suppose, in agreement with Meyer and Mark's X-ray investigations that the protein *collagen* consists of fibers built up of crystallites composed of primary valence chains of the anhydro-(peptided) amino-acids—the protein macromolecules. The formation of gelatin consists in the peptization of these fibers, but the primary valence chains become disoriented and separated; complexes of these chains, possibly in a partly oriented or smectic ordering bind water by dipole orientation. On this view, the molecules of gelatin are fundamentally identical with those of collagen, the difference being only in the degree of association and orientation."

* Communication No. 502 from the Kodak Research Laboratories.

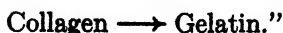
¹ Z. physiol. Chem., **2**, 299 (1878).

² Chem. Met. Eng., **23**, 5 (1920).

³ J. Biol. Chem., **3**, 33 (1907).

⁴ Sheppard and Houck: J. Phys. Chem., **34**, 273 (1930).

In the second paper⁵ Sheppard and McNally stated "the increase in optical anomaly obtained by stretching and drying gelatin jellies represents a movement in the direction of reversing the process:



It was pointed out that these results were in agreement with those of Katz and Gerngross⁶ on the similarity of the X-ray diagrams of collagen and of stretched dried gelatin. We shall discuss the deductions from X-ray spectrography later.

Absorption of Water by Collagen and Gelatin

The absorption of water by gelatin is very much greater than by collagen. The experiments of Sheppard and McNally⁷ showed that stretching gelatin jellies before drying decreased the subsequent swelling in water in the direction of the stretch. No considerable change in total water absorption was observed, but the actual elongations effected were not very large. We have produced subsequently very large elongations or distentions of gelatin jellies by the method of Katz and Gerngross (strips of jelly soaked 4-5 days in 60% alcohol-buffer mixture), of the order of 200% along the axis of stretch itself. Birefringence measurements on these showed that a very considerable degree of orientation had been effected.

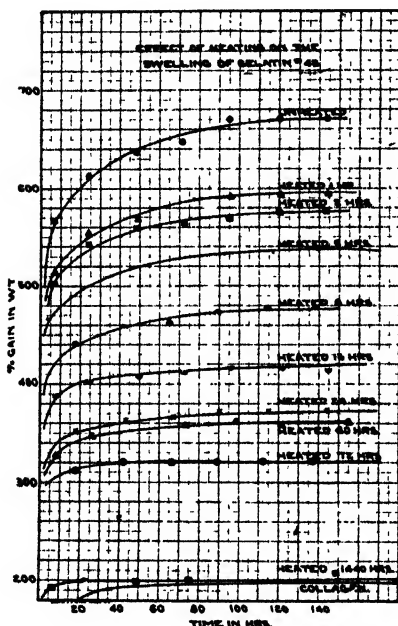


FIG. 1

(re-)orientation produced by stretching has assimilated gelatin to collagen in some respects, yet there remains a definite structural difference which allows (a) greater water absorption, and (b) solution in water at 40°C and above.

We have made, therefore, a study of the insolubilization of gelatin by heating at various temperatures.

Experimental

Gelatin strips of Eastman De-Ashed Gelatin No. 48 coated to 0.005" thick were used. (This gelatin contained 0.5% heat coagulable protein.) The strips

⁵ Sheppard and McNally: Colloid Symposium Monograph, 7, 17 (1930).

⁶ Kolloid-Z., 39, 180 (1926).

⁷ Loc. cit.

were heated for various increasing lengths of time, and the water absorption at 15°C was measured, the liquid being $M/1000$ acetic acid-sodium acetate buffer at pH 4.95, the isoelectric point of this gelatin. The buffer solution was changed daily, pH being determined electrometrically. The water absorption was determined at different times by weighing, until equilibrium was reached.

The results for heating at 105°-110°C are shown by Tables I-XI and in Fig. 1.

TABLE I

Water Absorption of Gelatin 48
(Heated at 105°-110°C)

Heated for 1 hour		Heated for 2 hours		Heated for 5 hours		Heated for 8 hours	
Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight
7.3	515	6.2	504	3.2	467	17.7	441
24.5	554	23.5	543	20.6	497	42.2	458
49.0	568	48.1	559	45.2	518	65.2	462
72.1	568	71.1	563	68.2	512	88.7	473
95.6	592	94.6	568	91.7	532	114.2	479
121.1	594	120.1	575	117.2	534	136.9	476
143.8	593	142.8	577	140.0	537		
Heated for 16 hours		Heated for 24 hours		Heated for 40 hours		Heated for 48 hours	
Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight
7.9	389	18.3	352	8.4	338	18.9	342
25.1	404	42.9	362	26.3	347	41.9	344
49.7	409	66.7	367	49.4	346	64.4	350
72.6	413	90.2	373	72.9	358	89.9	356
96.2	418	115.7	372	98.3	362	112.6	355
121.7	418	142.5	373	121.1	357	138.1	354
144.5	415			154.7	362	163.1	357
Heated for 72 hours		Heated for 1440 hours					
Time hours	% Gain in weight	Time hours	% Gain in weight				
18.0	311	6.1	193				
41.5	320	22.5	199				
65.9	320	46.8	199				
88.7	321	70.1	201				
112.1	315	147.6	205				
136.0	323	243.4	199				

As may be seen, the water absorption values decreased steadily with time of heating, approaching a limiting value after heating 2 months (ca. 1440 hours) of 199%. This value approaches closely that found for the limiting water absorption of collagen (from hide) which gave 200% regain. Reconditioning the heated material by exposure to air of approximately 50% R. H.

for 50 days produced practically no change in the water absorption. Furthermore, gelatin heated more than five hours at 106° to 110°C was incompletely peptized by warm water, the extent and ease of peptization falling off rapidly with further heating.

Order and Heat Increment of the Reaction

As a variable proportional to the concentration (or original gelatin) we have taken the "equilibrium per cent regain" for a sample of gelatin heated for time t , minus the "equilibrium per cent regain for infinite time." Calling this $C - C_\infty$, we found for C_∞ the value 200—as stated, the same as for collagen. On graphic analysis of the reaction curves, it was found that plots of $1/(C - 200)^2$ against time t yielded straight lines in the case of the three gelatins tested (Nos. 48 and 50 Eastman De-Ashed and No. 6432 Commercial). This corresponds to an equation of the form

$$1/x^2 = kt \quad \text{or} \quad dx/dt = k(a - x)^2$$

i.e., a termolecular reaction. The results for gelatin No. 48 heated at 107°C are shown in Table II.

TABLE II

Velocity of Insolubilization by Heat of Gelatin No. 48 at 107°C

Time Heated in hrs.	G % Gain in weight	G-200	1/G-200	1/(G-200) ²
0.0	668	468	2.13×10^{-3}	454×10^{-8}
1.0	593	393	2.54	645
2.0	576	376	2.65	702
5.0	537	337	2.96	876
8.0	476	276	3.62	1310
16.0	418	218	4.18	2097
24.0	372	172	5.81	3375
40.0	362	162	6.17	3806
48.0	355	155	6.45	4160
72.0	320	120	8.33	6938
1440	199	0		

To obtain the temperature coefficient of the reaction, the velocity constants were determined for different temperatures, using gelatins No. 50 and No. 6432.

At 60°C the rate of insolubilization was too small to be measured in convenient time, no appreciable change (diminution of swelling) being effected in 48 hours. Results obtained at 90°, 107° and 116°C for gelatin No. 50 are given by Tables III and IV and Figs. 3-7.

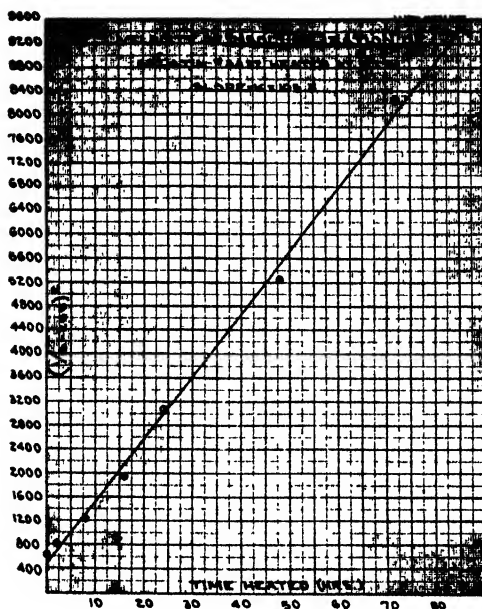


FIG. 2

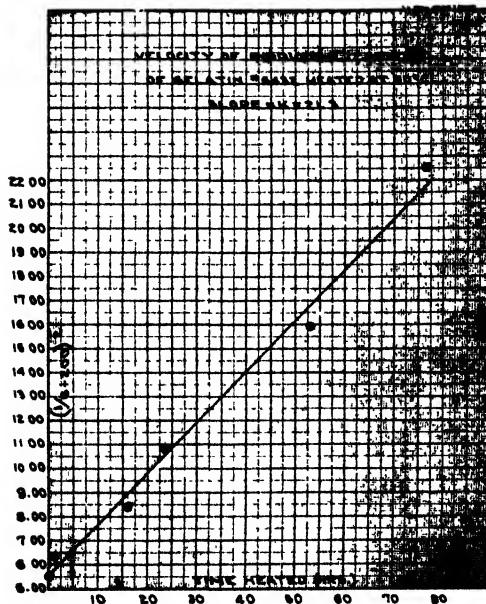


FIG. 3

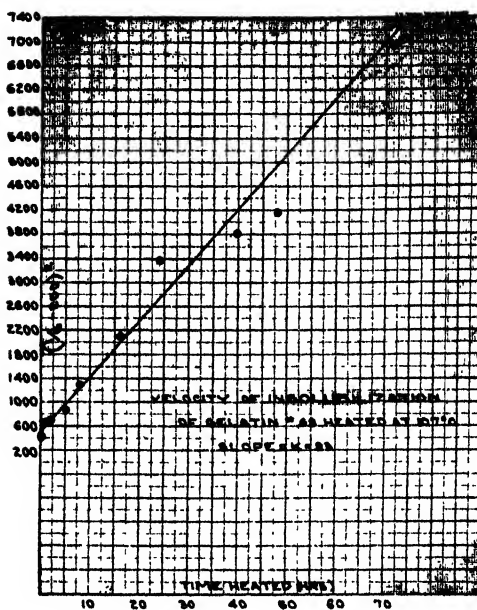


FIG. 4

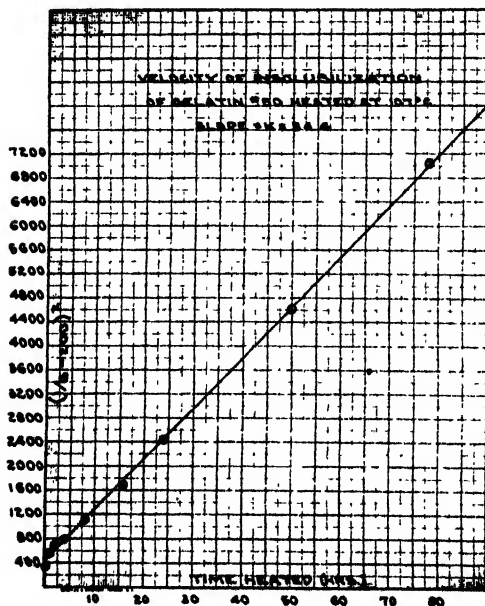


FIG. 5

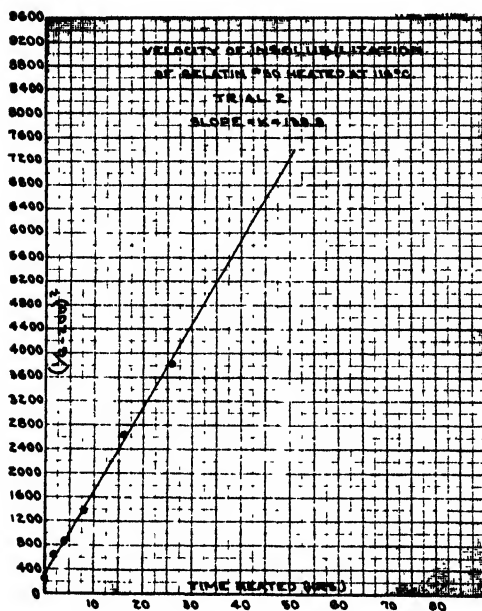


FIG. 6

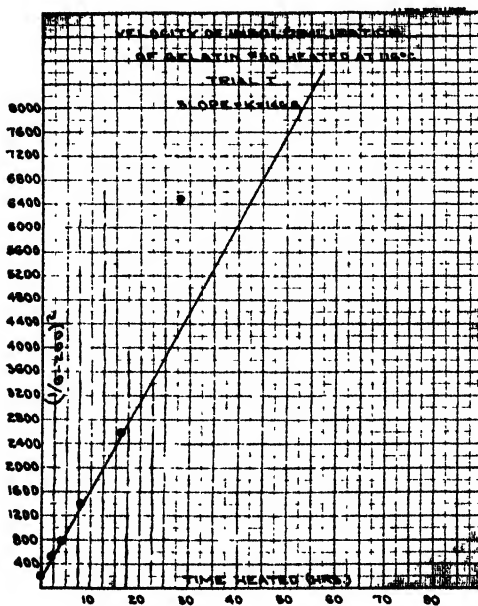


FIG. 7

TABLE III

Effect of Heating at 60°C on the Swelling of
Gelatin No. 50 + 4% Albumen

<u>Time Heated in hrs.</u>	<u>"Equilibrium" Water Absorption</u>
0.0	949
1.0	978
2.0	991
4.5	1000
8.0	906
16	956
24	942
48	952

TABLE IV

Velocity of Insolubilization of Gelatin No. 50 Heated at 90°C

<u>Time Heated in hrs.</u>	<u>G % Gain in weight</u>	<u>G-200</u>	<u>1/G-200</u>	<u>1/(G-200)²</u>
0	776	576	1.73×10^{-8}	299×10^{-8}
1	733	533	1.88	353
8	699	499	2.00	400
16	616	416	2.40	576
48	520	320	3.13	979
95	430	236	4.24	1798

It appears that the expression for the termolecular reaction holds with substantial accuracy for the whole course at 90° and 107°, and for a considerable part at 116°C. The deviation here is to be expected, since after 24 hours heating at this temperature the gelatin began to yellow and give signs of charring and decomposition.

In Table V are given the velocity constants at 90°, 107° and 116°C.

TABLE V

Velocity Constants of Insolubilization of Gelatin No. 50

<u>Temperature</u>	<u>Velocity Constant (Slope of 1/(G-200)² vs. time curve)</u>
90°C	18.6
107°	84.4
116°	146.6
	139.9
	166.6
	av. 150

Applying the Arrhenius expression for the effect of temperature on the reaction

$$\frac{d \ln K}{dt} = \frac{Q}{R T^2}$$

in the integrated form

$$\ln \frac{K_1}{K_2} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

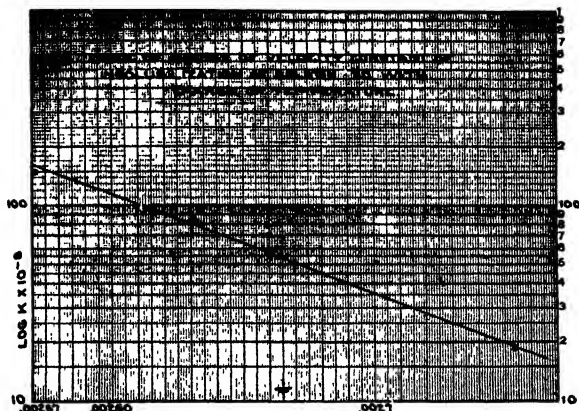


FIG. 8

then the "critical increment" Q should equal the slope of the $\log K$ vs. $1/T$ graph, multiplied by 2.303×1.98 . In Fig. 8 are plotted the data from Table V. This gives $Q = 23,159$ calories as the "critical increment." A further justification for the end value 200 is obtained from the effect of ultraviolet light in producing insolubilization, which shows much resemblance to insolubilization by heat. Brintzinger and Maurer⁸ measured the effect on degree of swelling. Using our value 200, and the termolecular expression, results shown in Table VI, and Fig. 9 were obtained, which indicate a close similarity in the reactions.

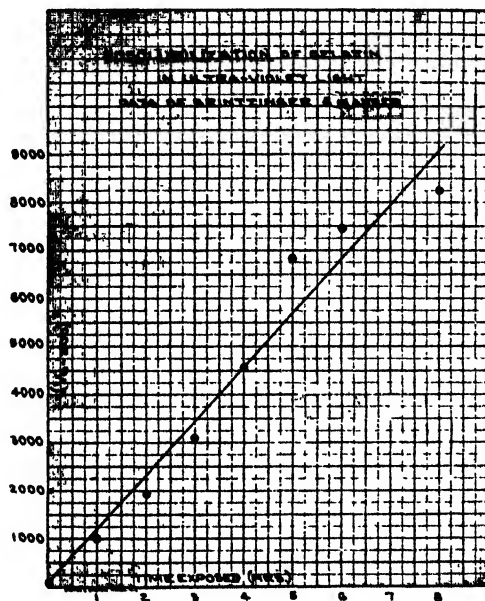


FIG. 9

⁸ Kolloid-Z., 41, 46 (1927).

TABLE VI
Velocity of Insolubilization of Gelatin by Ultraviolet Light
(Brintzinger and Maurer)

Time Exposed in hrs.	G	G-200	I	I
	% Gain in Wt.		G-200	(G-200) ²
0	1140	940	1.06×10^{-3}	112×10^{-8}
1	512	312	3.20	1024
2	426	226	4.42	1953
3	380	180	5.56	3091
4	348	148	6.76	4569
5	321	121	8.26	6822
6	316	116	8.62	7430
8	310	110	9.09	8262

The fact that the "equivalent temperature," corresponding to the very high velocity, lies much beyond the actual temperature to which gelatin could be heated without decomposition, does not contradict this. Many photochemical reactions correspond to thermal reactions at unrealizable temperatures.

Nature of the Insolubilization Process

Desiccation of gelatin in vacuo over P_2O_5 for prolonged periods produced not more than 5% decrease in water absorption. Apparently all "free" water was removed by evacuation to constant weight (upward of 10 days) which gave the same loss of water as heating at 105°C within the error of experiment (15.1% compared to 14.9% for samples starting at same R. H.). Again, insolubilization proceeds long after apparent constant weight has been reached.

While this indicates that probably the removal of free or adsorbed water is not responsible for the insolubilization, it does not preclude a condensation, *i.e.*, elimination of H_2O between reacting groups. First, the amount of this might be small enough to fall within the error of weighing so hygroscopic a material, and second, the primary adsorption of water by dried gelatin is so powerful that it would act as acceptor for the H_2O molecules thus split off. The insolubilized gelatin does not show optically (birefringence) any marked change compared with the dried gelatin. This indicates that no specific increase in orientation has occurred, which conclusion is confirmed by lack of local intensifications in the X-ray diffraction diagram.

The interpretation of a termolecular reaction course offers some difficulties. The variable is the difference between actual water absorbing capacity at time t and infinite heating. The assumption that this is directly proportional to active mass of unchanged gelatin seems reasonable, but gives no clue to the termolecular course.

If gelatin jelly is dried down to adhere on a rigid support, swelling, *i.e.*, water absorption, can only take place in one direction, *viz.*, that perpendicular to the plane of the support (Sheppard and McNally)⁹. The total water absorp-

⁹ Loc. cit.

tion, however, remains practically the same. Again, if gelatin jellies are stretched some 300% and dried while so stretched, the swelling or water absorption in the direction of stretch becomes negligibly small, but the total water absorption remains the same as for unstretched gelatin. It seems possible then that for actual reduction of *total* water absorption, a reaction in *three directions* or dimensions is necessary, and that this is the significance of

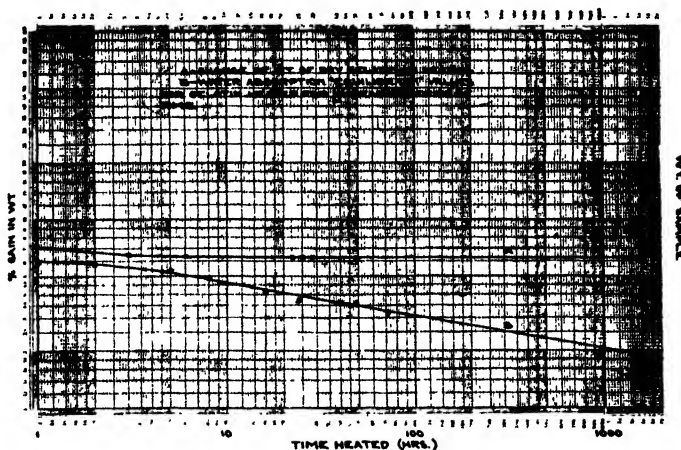


FIG. 10

the termolecular order. The following discussion of cognate evidence on the fine structure of proteins, in particular of gelatin, collagen and keratin, lends perhaps some support to this hypothesis.

Fine Structure of Proteins

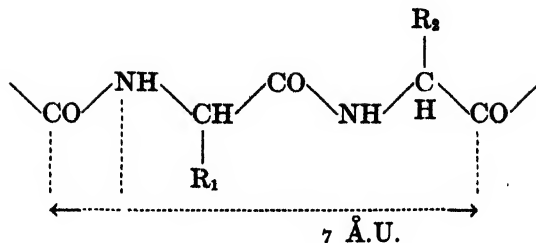
We shall understand by "fine structure" the molecular and micellar constitution of the proteins as revealed or indicated by chemical investigations, by X-ray spectroscopy, and by other investigations, such as Svedberg's centrifugal separation, spreading of thin films, and the adsorption and transpiration of gases and vapors. Chemical investigation has in the main confirmed Fischer's conclusion that the proteins consist of long chain-like molecules of condensed or peptided amino-acids, a typical polypeptide chain being



This does not preclude these chains in actual proteins being branched, nor that ring formation (by anhydridization between end groups) may occur.

This conception has been confirmed and made much more specific by recent X-ray investigations.¹⁰ Briefly, these indicate that the natural proteins consist of more or less uniformly oriented crystallites (primary micelles) of parallel polypeptide type chains. In the case of silk fibroin the chain may be represented as

¹⁰ Cf. Meyer and Mark: "Der Aufbau der hochpolymeren organischen Naturstoffe" (1930); Astbury and Woods: J. Textile Inst., **23**, T17 (1932).



It is the $-\text{C}-\text{NH}-\text{CH}-$ repeating unit which gives dimensional regularity and similarity, the side chains R_1 , etc., which in the first place provide differentiation. The following proteins have been found to give diagrams interpretable in this general sense:— silk fibroin,¹¹ keratin in wool and hair,¹² collagen in sinews,¹³ and to some extent in hide,¹⁴ gelatin.¹⁵ It is to be noted that all these belong to the so called sclero-proteins, not dispersing in water or aqueous solutions, with the exception of the derived protein, gelatin. Of these, silk fibroin is composed principally of glycine and alanine. Primary valence (polypeptide) chains of these in alternating order are arranged in parallel bundles as crystallites or micelles. There is also an amorphous, or non-oriented material which can be extracted with formic acid. For the crystalline part observations permit of the calculation of a monoclinic cell¹⁶ characterized as

$$a = 9.68 \text{ \AA.U.}$$

$$b = 7.00 \text{ \AA.U.}$$

$$c = 8.80 \text{ \AA.U.}$$

$$\beta = 75^\circ 50'$$

The interval $b = 7.00 \text{ \AA.U.}$ is the identity period along the fiber axis. The assumption of 4 alanyl-glycyl chains for the elementary cell leads to a density of 1.46, as compared with 1.33 to 1.46 observed. The distances of the principal chains from each other, $1/2 a = 4.8 \text{ \AA.U.}$ and $1/2 c = 4.4$ are as usually found.

Meyer and Marks¹⁷ remark that "Der hohe Zusammenhalt der Peptidketten und der Mizelle aneinander erklärt sich durch die besonders hohe Molkohäsion der CONH-Gruppe (10,600 cal)." Assuming that the molar cohesion of a glycyl residue is about 11,000 cal, a chain of 100 peptide residues of length of 350 \AA.U. would have a molar cohesion of over 10^6 cal, which approaches that of a cellulose chain. The similarity of silk and cellulose fibers in respect of tensile properties rests on analogous constitution and micellar (lattice) forces.

¹¹ Kratky: *Z. physik. Chem.*, **5**, 297 (1929).

¹² Astbury et al: *Loc. cit.*; Abitz: *Dissertation*, Leipzig (1930).

¹³ Herzog and Jancke: *Ber.*, **53**, 2162 (1920).

¹⁴ Gerngross and Katz: *Loc. cit.*

¹⁵ *Ibid.*

¹⁶ Cf. Meyer and Mark: *Op. cit.* p. 222.

¹⁷ *Op. cit.*, p. 223.

While cellulose and silk fibroin show no special features under mechanical or thermal treatment, rubber, keratin (of wool and hair), and collagen (sinew) exhibit notable peculiarities. Thus, rubber only shows a well defined fiber pattern on considerable stretching. On the other hand,¹⁸ keratin of wool and hair shows one pattern, with an identity period in the fiber direction of 5.1 Å.U. for unstretched material (α -keratin), and another for stretched material. The α -keratin chain of 5.15 Å.U. period appears to change into a chain with two definite halves when stretched to 6.64 Å.U., i.e., to show two halves of 3.32 Å.U. This extension of 29% corresponds to actual 30% extension. Its limits of elastic extension is 100%, close to 3×3.32 Å.U. This intramolecular displacement is diagrammatically typified in Fig. 11.

β -keratin, silk fibroin, and in some degree collagen, and stretched rubber have fully extended chains, while unstretched hair (α -keratin) and unstretched rubber, and, perhaps, *heated* collagen (sinew) have "folded" chains.

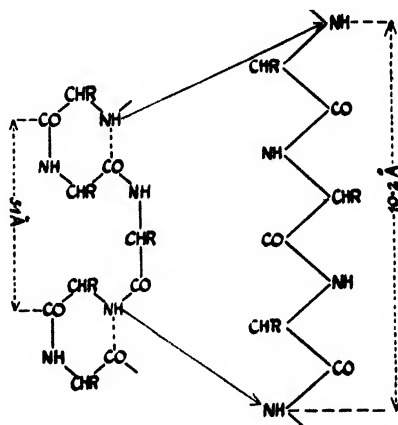


FIG. 11

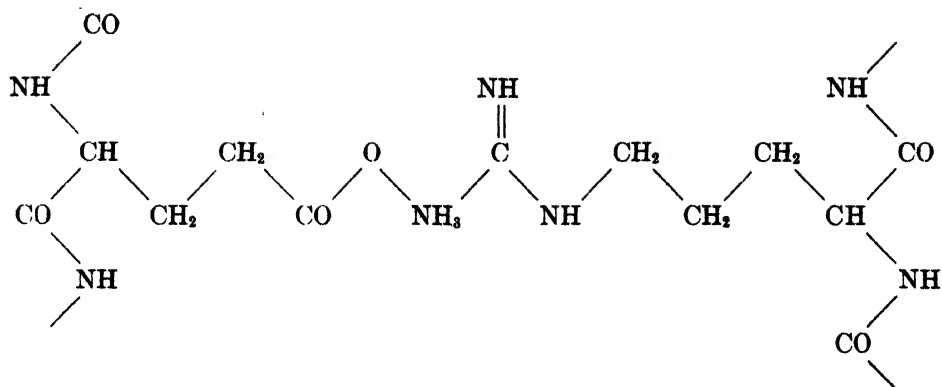
Intermolecular and Intramolecular Forces

The great strength of fibers is to be attributed to the intermolecular forces, or molar cohesion of the chains.¹⁹ It appears, however, that this, at any rate with the "extended" type of chains, is not enough to prevent intramolecular swelling by water, and, by reason of the consequent loss of molar cohesion, peptization and solution at sufficient temperature to destroy orientation. This is what occurs with gelatin, not only ordinarily dried gelatin, but gelatin *stretched 200 to 300%*, which gives a partly "fibrous" diagram practically identical with that from collagen. Yet collagen itself, though taking up 200% of water, does not peptize or dissolve in water at temperatures such as gelatin does, but requires nearly boiling water. There are a number of phenomena with these materials which make it a probable, if not a necessary assumption, that a certain degree of intramolecular binding occurs between chains. Speakman and Hirst²⁰ explaining the action of acids in lowering the work required to stretch wool fibers (compared to water at the isoelectric point) suggest linkages of the *free* amino groups of the diamino-acids—arginine and leucine—with the *free* carboxyl groups of dicarboxylic acids—aspartic and glutamins. This would give a bridge of the type

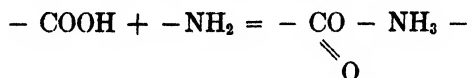
¹⁸ Astbury and Woods: Loc. cit.

¹⁹ Meyer and Mark: Loc. cit., p. 223.

²⁰ Nature, 128, 1074 (1931).



Evidence for an intermolecular period of -27 \AA.U. —about twice that given by the above, has been found by Astbury in wool, while Speakman shows that the heat of formation of the linkage



would be of the order of the work difference of stretching in acid and water -1.2 kg calories . Astbury and Woods²¹ have also suggested cross linkages of sulfur atoms (from cystine) and of anhydrides of the free carboxyls of dicarboxylic acids.

So far, these interlinkages have been proposed as occurring between the parallel chains of the crystallites proper. This should be capable of verification by X-ray spectroscopy in conjunction with swelling experiments. Attention may be drawn to the possibility of condensations and interlinkages occurring between the fringe-like ragged or unoriented extensions of the crystallites, evidence for the existence of which exists to some extent in the so-called amorphous, non-crystalline portions of fibrous materials.²²

It appears to us that such interchain or intermolecular linkages may be assumed to account for the difference between collagen and gelatin. The relatively high critical increment indicated by the temperature velocity coefficient points to more than a neutralization of $-\text{NH}_2$ by $-\text{COOH}$ groups. It is true that this heat value— $25,000 \text{ cal.}$ —probably does not refer to a specific heat formation of a substance or linkage. If the reaction is a condensation, the “critical increment” from kinetic considerations will be the sum, or difference, of heats of activation and true heat of reaction (heat of formation of products). If the insolubilization of gelation by ultraviolet—necessarily of wave-length shorter than 3600 \AA.U. —may be regarded as involving a quantum of that order for activation, this would mean about $70,000\text{--}90,000 \text{ cal.}$, which is of the same order as the predissociation energies of certain organic molecules.

²¹ Loc. cit.

²² Cf. Abitz: Roentgenographische Strukturforchung des Gelatine-micells. Dissertation, Leipzig (1930).

On this view the actual reaction concerned in the insolubilization of gelatin would be generating heat, but considerably less than the activation heat required.

The Effect of Additions on the Insolubilization of Gelatin

It has been suggested by Northrop and Kunitz²³ that the swelling phenomena of gelatin in water at the isoelectric point can be interpreted in terms of the osmotic pressure of a soluble gelatin encased in capsules of an "insoluble" gelatin. Evidence has been produced by Sheppard and Hudson²⁴ that the insoluble gelatin fraction separated by Kunitz and others is an albuminous impurity, occurring in amounts varying from 0.2 to 1.5% in commercial gelatin. It has a different chemical composition, and is coagulated by heat in weakly acid solution (pH 4.7). The present authors expect to publish data showing other difficulties for this theory of swelling. The possibility, however, that the observed insolubilization of gelatin might depend upon a coagulation of this dispersed albumin in gelatin led us to test the effect of addition of

(a) egg albumin

(b) gelatin albumin

upon the heat insolubilization. The results did not support the view that the insolubilization of gelatin is in any way caused by coagulation of a foreign protein.

Insolubilization and Denaturation

In some respects the insolubilization of gelatin might be assimilated to the coagulation and denaturing of albumins. Miss Galinsky²⁵ in an interesting paper on "The Effect of Light and Salts on Gelatin" states that exposure of a dichromated gelatin solution to light, followed by precipitation in acetone, gives an insoluble gelatin which is ash-free, *i.e.*, contains no chromium. This gelatin was chemically indistinguishable from the soluble original, and its production is regarded as similar to the coagulation of albumin. We hope to compare this insoluble gelatin with that produced by direct action of heat and of light. Provisionally it appears probable that the dichromate first acts as a photochemical (optical) sensitizer for the insolubilization, and is subsequently reduced.

Gelatin insolubilized by heat may be reverted, *i.e.*, converted to soluble gelatin, by treatment with boiling water. The regenerated gelatin had similar but slightly higher swelling values than the original. We shall show elsewhere that this is probably caused by a greater proportion of hydrolyzed gelatin.

Summary

Gelatin on prolonged heating at sufficiently elevated temperatures progressively loses swelling power and its solubility in warm water. A quantitative study has been made on this behavior; the results extend the conception of collagen and gelatin as high molecular compounds and clarify their rela-

²³ Kunitz and Northrop: *J. Gen. Physiol.*, **12**, 384 (1928).

²⁴ Sheppard, Hudson and Houck: *J. Am. Chem. Soc.*, **53**, 760 (1931).

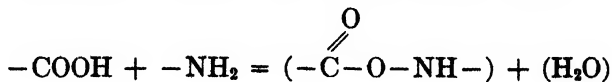
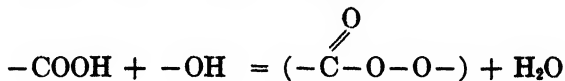
²⁵ *Biochem. J.*, **24**, 1706 (1931).

tionship. The rate of insolubilization, as measured by reduction of swelling capacity (water absorption) is a marked function of temperature. The reaction follows a termolecular order; from the temperature coefficient, in the Arrhenius expression $\frac{d \ln K}{dt} = \frac{Q}{R T^2}$, Q the critical increment of insolubilization was found to be 23,160 calories.

Insolubilization by ultraviolet light was found to follow the same reaction course, though at greater velocity than that at the highest temperature studied (116° C).

The insolubilized gelatin resembles collagen (a) in having the same water absorption, and (b) in being converted to gelatin by extraction with hot water. It differs in not showing the X-ray diagram of collagen, nor optical birefringence. If gelatin jellies (made with much alcohol) are stretched several hundred percent, and dried at room temperature, the dried material is optically anisotropic and gives the X-ray diagram of collagen. Although it swells very little in the direction of stretch, its total water absorption is the same as for unstretched gelatin. By heating this stretched gelatin to insolubilization, a material is produced having substantially all the physical characteristics of collagen.

It appears probable, therefore, that the conversion of collagen to gelatin involves something more than the disorientation of long chain molecules assembled in crystallites. The facts suggest hydrolytic disruption of definite chemical interlinkages between these long chains. These linkages, causing some degree of two-dimensional and three-dimensional polymerization or macromolecule formation, confer insolubility and greatly restricted intramolecular water absorption. A reaction of the types



between side groups of the primary molecular chains would account for the phenomena; they would thereby be brought into line with the vulcanization of rubber, the "permanent set" of steamed hair, and perhaps other changes in high molecular substances.

Rochester, N. Y.

COLLOID CHEMISTRY OF ASPHALTS

BY CHARLES MACK

Zsigmondy made the following statement—"we are accustomed in chemistry to ask investigators who speak of the existence of a chemical compound to give proofs of its existence, its make-up, and its detailed description." In the application of this statement to asphalts, we find that our knowledge of this material is very poor and empirical.

If we consider asphalt as belonging to the realm of colloid-chemistry, it must be studied from both the chemical and physical aspect, since the colloidal state is an intermediate one between physics and chemistry.

Chemistry of Asphalts

According to Marcusson¹ asphalt is composed of five groups of compounds: Oily constituents; asphaltic resins; asphaltenes; carbenes and carboids; asphaltic acids and anhydrides.

Oily Constituents. The oily constituents may be separated from asphalt by first mixing the latter with Fuller's earth or some adsorption clay and then extracting the mixture with petroleum ether. These compounds appear as a viscous oil similar to cylinder oil and are usually fluorescent. They are hydrocarbons, and generally contain small percentages of sulphur and oxygen.

Asphaltic Resins. The asphaltic resins represent the intermediate products formed in the transformation of oily constituents into asphaltenes by oxidation with air. They are solid with a softening point of 100° C or higher. They vary from reddish to dark brown in colour. When adsorbed by clay they cannot be extracted with petroleum ether. The adsorption clays polymerize the asphaltic resins with partial formation of asphaltenes. The best method for their separation is due to Sachanen.² The asphaltic acids are first of all extracted from a solution of asphalt in 5 parts of benzene by means of alcoholic potash solution. After having washed out the benzene layer with water the asphaltenes are precipitated with petroleum ether. The remaining solution which contains the resins and oily constituents is treated with silica gel in the ratio of 100 parts of silica gel to 1 part of resins. The oily constituents are extracted with light naphtha and the adsorbed resins with chloroform.

Sachanen found that the molecular weights of the resins depend upon the molecular weights of the oils from which they are derived, and that they are always somewhat higher than the molecular weights of the oily constituents. The resins contain oxygen and are oxidation products of the oily constituents and not products of condensation. Resins form true solutions with certain solvents.

¹ "Die naturerlichen und kuenstlichen Asphalte" (1931).

² Sachanen and Wassiliew: *Petroleum Zeit.*, 23, No. 36, 1618 (1927).

Asphaltenes. Asphaltenes are formed from asphaltic resins by further action of sulphur or oxygen. They appear as a dark brown to black powder. On heating they do not melt but swell. Their specific gravity is higher than 1. They are soluble in benzene, chloroform, carbon tetrachloride and insoluble in ether, petroleum ether and alcohol. Before they dissolve in the solvents mentioned above they swell. By evaporation of these solutions homogeneous solutions of high concentrations can be obtained which set to gels at lower temperatures. In contrast to the asphaltic resins the asphaltenes form colloidal solutions.

Chemically speaking, the following reactions are characteristic for asphaltenes as well as for asphaltic resins: When treated with fuming nitric acid they are changed into nitro-compounds soluble in acetone, which after treatment with alcoholic potash solution become soluble in water. The alkali salts of these nitro-compounds are precipitated by calcium chloride, silver nitrate, etc.

Asphaltic resins and asphaltenes form addition products with sulfuric acid. They are oxidized by potassium permanganate to acids. They do not react with diazo-compounds nor with phosphorus pentachloride, but form molecular compounds with mercuric bromide and ferric chloride. They cannot be saponified and show only small acetyl numbers. According to these properties asphaltenes and asphaltic resins do not appear to react like acids, esters or lactones, or to contain alcoholic or phenolic hydroxy or oxy-groups.

Poell³ has shown that the determination of iodine numbers on asphalts and lubricating oils have no meaning since the amount of iodine taken up can be found as hydriodic acid. This would indicate that no double bonds are present, and that in these cases iodine substitutes hydrogen. The chemical properties of the asphaltenes and asphaltic resins seem to indicate that they are polycyclic compounds containing oxygen and/or sulfur in bridge or heterocyclic linkage. Generally speaking, however, it is difficult to definitely establish the structure of compounds of high molecular weight from their chemical reactions.

Carbenes and Carboids. These compounds are present in petroleum asphalts only in minute quantities. Whereas, the carbenes are soluble only in carbon bisulphide, the carboids are totally insoluble in all solvents. They are obtained when asphalt is dissolved in cold carbon tetrachloride. The material insoluble in this solvent represents a mixture of carbenes and carboids. The solubility of the carbenes in carbon bisulfide is used as a means of separating them from the carboids.

In their chemical reactions with sulfuric acid, nitric acid, ferric chloride, mercuric bromide, etc. the carbenes and carboids behave like asphaltenes, and appear to be condensation or polymerization products of asphaltenes.

Asphaltic Acids and Their Anhydrides. They are present in petroleum asphalts in small percentages only, in contrast to natural asphalts, which contain them in larger percentages, as high as 12%. The asphaltic acids are separated from asphalts by cold extraction of a solution of asphalt in benzene

³ *Petroleum Zeit.*, 27, No. 45, 817-826 (1931).

with alcoholic potash solution. Having removed the asphaltic acids their anhydrides can be extracted as acids from the asphalt solution in benzene after saponification.

The asphaltic acids are brownish black in colour and form a tar-like or resinous mass usually containing sulphur. When heated to 120°C they are converted into the corresponding anhydrides and at higher temperatures are transformed into unsaponifiable substances.

Colloid Chemistry of Asphalts

The three main constituents of asphalts are asphaltenes, asphaltic resins and oily constituents. Asphalt forms a lyophilic sol. In our investigations we have considered the asphaltenes as the dispersed phase and the mixture of asphaltic resins and oily constituents as the dispersion medium. For simplicity this mixture of asphaltic resins and oily constituents will be referred to as "petrolenes," the term which is generally used.

Lyophilic Sols are characterized by: (1) Their relative stability; (2) difficulty in detecting particles of the disperse phase under the ultramicroscope; (3) high viscosity, often exhibiting elastic properties; (4) the property of forming gels; (5) low solubility of the solute in the solvent at the temperature of gel formation.

With respect to the first characteristic, asphalts generally represent a stable system. Investigations by Holde⁴ have shown that asphaltenes in solution are amicroscopic under the ultra-microscope.

Viscosity of Asphalts

One of the most important properties of asphalts is viscosity, since in practice the specifications for asphalts are generally expressed in terms of viscosity such as softening point and penetration. The softening point is defined as the temperature at which an asphalt that has been poured into a brass ring of standard size becomes soft enough to allow a steel ball of standard size to fall through it. The penetration of an asphalt is the distance measured in tenths of millimeters which a needle loaded with 100 grams will penetrate during 5 seconds under standard temperature conditions.

Penetrations are generally taken between 0 and 37.8°C. The viscosities of the asphalts studied were determined over the same temperature range since their viscosities at these temperatures are of importance with respect to their behaviour on the road.

For the determination of viscosity at low temperature, Pocchetino's falling cylinder apparatus⁵ has been used. The apparatus consists of two vertical coaxial cylinders, the clearance between the cylinders being 0.0075 cm. The asphalt is poured between the cylinders to a certain height. The inner cylin-

⁴ Z. angew. Chem., 21, 2143 (1908).

⁵ Nuovo Cimento, 8, 77.

der is loaded with weights and the velocity with which it descends is measured. The viscosity is calculated from the following integrated formula:

$$N = \frac{P}{2\pi L v} \ln \frac{R_2}{R_1} \quad (1)$$

where N = viscosity in poises; P = total weight; v = velocity; L = length of tube of asphalt; R_2 = radius of outer cylinder; R_1 = radius of inner cylinder.

To study the influence of the concentration of asphaltenes upon the viscosities of asphalt, the asphaltenes were separated from the mixture of asphaltic resins and oily constituents (petrolenes) in the following way:

The asphalt was shaken with 50 parts of petroleum ether until the petrolenes were dissolved and the solution was then allowed to stand for 48 hours

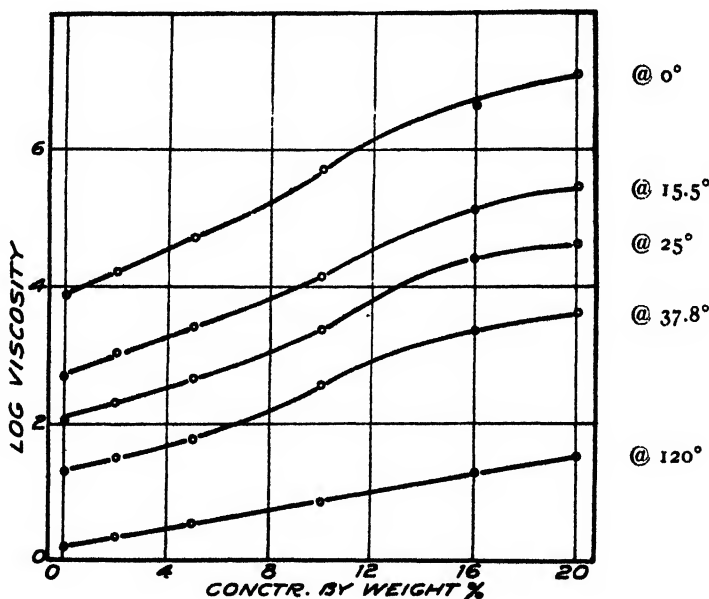


FIG. 1

Solutions of Asphaltenes in Petrolenes log. visc. vs. concentration. Visc. at 120°C in poises, visc. between 0 and 37.8°C in gr. sec. cm⁻².

in the dark. The extract was filtered from the asphaltenes. The asphaltenes were washed with petroleum ether until the filtrate was colourless. To free the asphaltenes from the last traces of resins they were dissolved in 10 parts of benzene and precipitated with 100 parts of petroleum ether. The procedure was then repeated. The different extracts of the asphaltenes were combined and filtered through an ultra-filter in an atmosphere of carbon dioxide. The ultra-filter was prepared from a hard filter paper by first treating it with a 2% solution of collodion in an ether-alcohol mixture and while still wet, coagulating the collodion with petroleum ether. The filtrate was then freed from the solvent by distillation removing the last traces under vacuum at 200°C. The petrolenes thus prepared were found to be free from asphaltenes.

In Table I, the viscosities are shown for mixtures of asphaltenes and petroleues obtained from a blown Mexican asphalt of a softening point of 64°C. Asphaltenes separated by the usual method from asphalt must be kept in solution in benzene because if they are dried after precipitation with naphtha they cannot be re-dissolved in the petroleues.

Structural viscosity has not been found to occur in these mixtures. By loading the inner cylinder of the falling cylinder apparatus with different weights, thus varying the velocity gradient, the same viscosity coefficients were obtained, within the allowable experimental error. The discontinuity of the log viscosity-concentration curves (Fig. 1) would indicate that structural viscosity occurs at concentrations between 10 and 20%. However, a sphere of about 1 cm diameter of the mixture containing 20% of asphaltenes spreads in about 5 hours on a plate at room temperature, indicating that this mixture is a liquid of high viscosity and not a plastic material.

From Table II it will be readily seen that relative viscosity increases with falling temperature and increased percentage of asphaltenes, *i.e.*, at 0°C from 2.13 for a 2% sol to 1792 for a 20% sol.

From this fact, and taking into consideration the formation of colloidal solutions of asphaltenes in benzene, it may be concluded that the asphaltenes are present in asphalts in colloidal state in the form of the emulsoid type. The concept of asphalts being stable suspensoid sols must necessarily be rejected, since the temperature coefficient of relative viscosity in lyophobic sols is merely that of the dispersion medium.

TABLE I
Viscosity of Sols of Asphaltenes in Petroleues in Poises

% Asphaltenes	@ 0°C	@ 15.5°C	@ 25°C	@ 37.8°C	@ 120°C
0%	7.44×10^6	4.70×10^5	1.10×10^5	1.86×10^4	1.645
2%	1.59×10^7	1.03×10^6	2.00×10^5	2.89×10^4	2.226
5%	5.03×10^7	2.48×10^6	4.65×10^5	5.59×10^4	3.437
10%	5.35×10^8	1.35×10^7	2.20×10^6	3.61×10^5	7.094
16%	4.44×10^9	1.38×10^8	2.22×10^7	2.17×10^6	18.85
20%	1.33×10^{10}	2.79×10^8	4.03×10^7	4.18×10^6	33.11

TABLE II
Relative Viscosities of Asphaltenes in Petroleues

% Asphaltenes	0°	15.5°	25°	37.8°	120°
2	2.137	2.136	1.82	1.552	1.353
5	6.76	5.281	4.23	3.00	2.09
10	71.82	28.81	20.01	19.37	4.312
16	596.4	294.1	201.8	116.2	11.45
20	1792.3	592.9	367.0	224.2	20.12

The Concentration Function

Since relative viscosity is a function of particle size, an attempt was made to apply several of the formulae dealing with the relationship between relative viscosity and concentration.

By a re-arrangement of Einstein's formula

$$N_s = N (1 + 2.5 c) \quad (2)$$

where N_s = viscosity of suspension; N = viscosity of dispersion medium; c = concentration of dispersed phase expressed as volume of suspensoid in unit volume of suspension, we obtain

$$N_s/N - 1 = 2.5 c \quad (3)$$

The expression on the left hand side of the equation represents "relative viscosity - 1" and is the viscosity by which the viscosity of the dispersion medium is increased under the influence of the dispersed phase. Staudinger⁶ calls this expression "specific viscosity" and denotes it by means of the following formula:

$$N_{\text{spec}} = c K_m M \quad (4)$$

where N_{spec} = specific viscosity; c = concentration; M = molecular weight of the solute; and K_m = a constant which has to be determined from viscosity data of the lower members of homologous rows.

The application of this formula to the viscosity data of asphalt may be best illustrated by means of an example. The values of N_{spec}/c for a 2% solution of asphaltenes in petroleums are 0.176 at 120°C and 1.068 at 0°C. Since K_m is a constant the molecular weight of the asphaltenes must be 1.068/0.176 = six times higher at 0°C than at 120°C. It is evident that this is impossible with relative viscosities of 2.137 at 0°C and 1.353 at 120°C.

Arrhenius' formula⁷

$$N/N_0 = K^c \quad (5)$$

in which N_0 = viscosity of solvent; N = viscosity of solution; c = concentration; K = a constant, does not take into consideration the molecular weight of the solute, and has not always been found to agree with the facts.

Kendall and Monroe⁸ have chosen compounds which form ideal solutions to ascertain the relation between viscosity and concentration. They have carried out viscosity measurements on naphthalene solutions in benzene and toluene at 25°C. The freezing points of these solutions have been determined by these investigators and found to be in agreement with the law of ideal solutions. Kendall and Monroe derived from their measurements a formula showing the viscosities of the solvent and of the solute to be additive which was found to give good results for the viscosity concentration relationship. However, since the viscosity of the solute differs with different solvents, this relationship has no meaning at all.

⁶ Ber., 63, 222 (1930).

⁷ Medd. Vetenskapsakad. Nobelinst., 3, No. 21 (1917).

⁸ J. Am. Chem. Soc., 39, 1802 (1917).

It was therefore very desirable to develop a formula connecting viscosity with concentration from which the molecular weight of the solute could be calculated. As far as it is known, a valid formula of this kind has not yet been published.

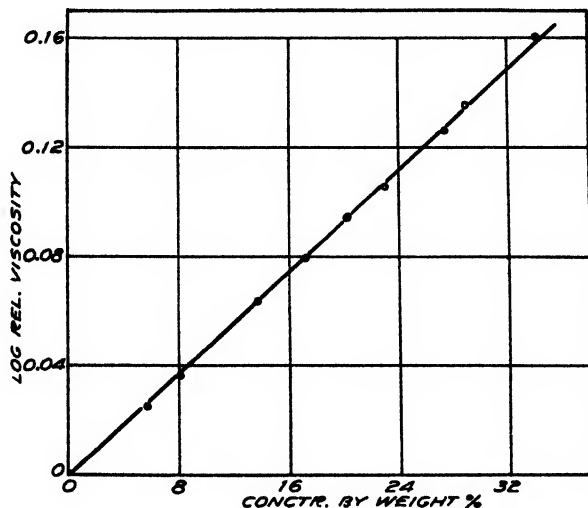


FIG. 2

Log. relative viscosity vs. concn. in percent by weight.

- Naphthalene in Benzene
● Naphthalene in Toluene

TABLE III

Viscosities of Solutions of Naphthalene in Benzene and Toluene in Centipoises (Temp. 25°)

(Kendall and Monroe)

Naphthalene in Benzene		Naphthalene in Toluene	
% of solute in solution	Absolute viscosity in c.p.	% of solute in solution	Absolute viscosity in c.p.
0.0	0.6048	0.0	0.5526
8.11	0.6565	5.73	0.5848
17.16	0.7261	13.72	0.6394
22.97	0.7707	20.12	0.6866
28.82	0.8263	27.31	0.7470
34.10	0.8764		

For these investigations Kendall and Monroe's data on naphthalene solutions has been chosen (Table III).

It has been found that when the logarithms of the relative viscosities for the solutions of naphthalene in benzene are plotted against concentration, a straight line is obtained upon which the logarithms of the relative viscosities for naphthalene in toluene are found to fall (Fig. 2). Since the straight line goes through the zero point the mathematical expression for the viscosity

concentration curve is $y = e^{ax}$, and the formula for the viscosity concentration relationship reads

$$\log \text{rel. viscosity} = c K \quad (6)$$

where "c" is the concentration in weight percent and "K" a constant.

The same formula is also obtained in another way. The logarithms of the absolute viscosities for these solutions plotted against concentration form a straight line. The absolute viscosities of solutions as a function of the concentration can be represented by $y = ae^{kx}$. Since "a" is a function of "y" when $x = 0$, the exponential equation reads $y = y_0 e^{kx}$. By applying this equation to viscosities and using the logarithmic form we obtain

$$\log N = \log N_0 + c K \quad (7)$$

$$\text{and} \quad \log N - \log N_0 = c K \quad (8)$$

which is the same as formula (6).

TABLE IV
K for Naphthalene Solutions

In Benzene		In Toluene	
% Naphthalene	K	% Naphthalene	K
8.11	0.004392	5.73	0.004293
17.16	0.004626	13.72	0.00461
22.97	0.004584	20.12	0.004636
28.82	0.004702	27.31	0.004793
34.10	0.004724	Average for K = 0.004609	

TABLE V
Viscosities of Diphenyl Solutions

In Benzene			In Toluene		
% Diphenyl	Viscosity	K	% Diphenyl	Viscosity	K
0	0.6051		0	0.5526	
18.08	0.7585	0.005427	21.38	0.7335	0.005752
30.57	0.9014	0.005662	Average for K = .005614		

The data of "K" for the naphthalene solutions tabulated in Table IV shows good agreement, and the same holds for solutions of diphenyl in benzene and toluene (Table V) the viscosity data of which has also been taken from the work of Kendall and Monroe.

Since the concentration by weight percent has been considered with respect to the relative viscosity, the constant "K" must be a function of the molecular weight

$$K = k.M \quad (9)$$

and formula (6) becomes

$$\log \text{relat. viscosity} = c.k.M \quad (10)$$

where " k " denotes a universal constant and " M " molecular weight. The molecular weights of two different compounds must be in the following ratio:

$$\frac{M_1}{M_2} = \frac{\log \text{rel visc}_1 c_2}{\log \text{rel visc}_2 c_1} = \frac{K_1}{K_2} \quad (11)$$

For diphenyl ($M_1 = 156$) and naphthalene ($M_2 = 128$) the calculations of both sides of the equation give the value 1.2.

The value for " k " has been calculated and found

$$k = 3.6 \times 10^{-5}$$

Formula (10) has been tested on different viscosity data of solutions and has been found to be as accurate as the cryoscopic method for determination of molecular weight (Table VI).

TABLE VI

	% By-Wt.	Rel. Visc. @ 25°	k.M	M	M Calculated	Error
Sucrose in water	13.03	1.3083/0.8953	0.01264	342.1	351	+2.6%
Benzyl-benzoate in toluene	41.69	1.183/0.552	0.00794	212.1	220	+3.7%

That the uniformity of the solvent has no influence upon the validity of this method may be seen from viscosity measurements of naphthalene dissolved in mineral oil. The viscosities were taken at 70°C and the mineral oil had an average molecular weight of about 300.

	%	Time of flow in (sec.)	Spec. Gravity	log time of flow + log spec. grav.
Mineral Oil		44.5	0.8473	1.57640
Naphthalene in Mineral Oil	17.3	37.0	0.8514	1.49833

The log relative viscosity would be $0.92193 - 1$, a negative figure, which corresponds to a negative value for k . Putting both negative figures in formula (10) and multiplying both sides with -1 we obtain for $k.M = .00451$, from which a molecular weight of 125.3 for naphthalene is calculated, which differs from the real molecular weight 128.1 by 2.2%.

In cases where the logarithm of the relative viscosity is not a straight line function of the concentration, association and/or solvation may be assumed.

In cases where solvation occurs, the degree of solvation can be calculated from formula (10) assuming that the molecular weight of the solute is known and that the solute is not associated.

$$\log \text{rel. viscosity} = c.f^2.k.M \quad (12)$$

where " f " is the solvation factor by which the concentration and also the molecular weight of the solute has to be multiplied to obtain the concentration which is composed of solute plus solvent.

It is generally accepted that gel formation and high relative viscosities of sols of lyophilic colloids are caused by solvation. If solvation is considered as a chemical combination between solute and solvent or as some form of attachment of the solvent to the dispersed phase, it can only occur in cases where both components are polar. There are however substances which show the same phenomena of colloids in non-polar solvents such as benzene. Hence solvation in this case can be considered as a solution process, which also applies to true solutions. Thus it seems that the term "solvation" is rather an indefinite one in its meaning.

The polar substances present in asphalts are the asphaltenes and asphaltic resins since they form molecular compounds with ferric chloride and mercuric bromide. Since asphaltenes are soluble in asphaltic resins (Sachanen⁹) and from other reasons to be discussed later, both groups were studied from the viewpoint of solvation. The procedure was as follows: 2 g of asphaltenes were shaken for 30 minutes with 1, 2 and 3 g of resins dissolved in petroleum ether to give a final volume of 100 cc. After centrifuging the concentrations were determined. In order that equal particle size of the asphaltenes could be obtained in each case, the asphaltenes (2 g) were dissolved in 10 cc. of benzene and precipitated by slowly adding sufficient petroleum ether to give a total volume of 200 cc. The precipitated asphaltenes were separated by centrifuging for 20 minutes. The liquid was decanted, and the asphaltenes were shaken with 200 cc. of petroleum ether and centrifuged again.

From a consideration of the system "asphaltenes-resins" there are three possibilities: (a) Formation of a chemical compound, the amount of resins combined with the asphaltenes must be constant; (b) solutions of the resins in the asphaltenes; Henry's law of distribution must be obeyed. (c) Adsorption of the resins at the surface of the asphaltenes according to Freundlich's law

$$a/m = Kc^{1/n} \quad (13)$$

where a = weight of the adsorbed material in g; m = adsorbent in g; K and n = constants.

The data shows that cases "a" and "b" are not found to hold—

No.	Amt. of resins g	Amt. of asphaltenes g	c_1 Concen'n. of resins in asphaltenes %	c_2 Concen'n. of resins in pet. ether %	c_1/c_2
1	1	2	13.64	0.7420	18.38
2	2	2	21.36	1.6048	13.31
3	3	2	23.77	2.5760	9.22

By the application of Freundlich's law to the results obtained, and by dividing the equations for 2 in 1 and for 3 in 4, the calculated values for $1/n$ are equal to 0.58 and 0.57, indicating that the resins are adsorbed by the asphaltenes. In 3 the saturation point is almost reached and a further addition of resins would not increase the amount of resins adsorbed by the asphaltenes.

⁹ Petroleum Zeit., 21, No. 23, 1442 (1925).

Since surface phenomena have a predominating influence it can be assumed that the distribution law is masked by them, and that adsorption is a limited case of solution.

The petrolenes from the Mexican asphalt under investigation represent a solution containing 30.6% of resins and 69.4% of oily constituents. In the asphalt mixture containing 20% of asphaltenes 24.48% of resins are present, and we may assume that in this system also 23.77% of the resins as in 3 are combined with the asphaltenes due to solvation. Since the concentration as well as the molecular weight are both 1.23 times higher when solvation is assumed, the logarithm of the relative viscosity must be 1.51 times higher to conform with formula (12). Taking the logarithm of the relative viscosity at 120°C as base, the corresponding logarithms of the relative viscosity are 1.8 times higher at 37.8°, 2.0 at 25°, 2.12 at 15.5°, and 2.5 times higher at 0°. These values are too high to account for solvation, and it is more reasonable to consider high relative viscosity as a result of association of the molecules of the solute, due to the inability of the solvent to overcome the space lattice forces which cause the polymeric bond.

The data of $k.M$ and M according to formula (10) for the different solutions of asphaltenes in petrolenes are given in Table VII. It will be readily seen that the asphaltenes are in true solution at 120° and associate with decreasing temperature, and that the degree of association increases to a certain concentration only to decrease again. This is in accord with the fact that polar substances in solution which associate to form chain molecules (the dipole moment is increased) may obtain their highest polarity at a certain concentration, which differs with different temperatures.

The average molecular weight of 1800 for the asphaltenes calculated from the relative viscosities indicates that the asphaltenes must be considered as hemicolloids.

TABLE VII

% Asphalt tenes	k.M	Degree of Assoc.	@ 0° M	k.M	Degree of Assoc.	@ 15.5° M	k.M	Degree of Assoc.	@ 25° M
2	0.16496	2½	4580	0.1698	2½	4710	0.1301	2	3610
5	0.1650	2½	4580	0.1446	2½	4010	0.12531	2	3480
10	0.1856	3	5160	0.1459	2½	4050	0.13012	2	3610
16	0.17347	2½	4820	0.15428	2½	4280	0.14405	2½	4000
20	0.16267	2½	4520	0.13865	2½	3850	0.12823	2	3560

% Asphalt tenes	k.M	Degree of Assoc.	@ 37.8° M	k.M	@ 120° M
2	0.09553	1½	2650	0.06568	1820
5	0.09542	1½	2650	0.0640	1780
10	0.12871	2	3580	0.0635	1760
16	0.12907	2	3580	0.0662	1830
20	0.11753	1½	3260	0.0652	1810

Average M = 1800

Sachanen² determined the molecular weight of asphaltenes in benzene by the cryoscopic method and found values of 5-6000. The molecular weights of the asphaltenes from oxidized Mexican asphalt determined by the same method have been found to be of the same order. However, it was observed in one case that partial separation of the two phases took place. Molecular weights of the same asphaltenes in benzene solution determined by the viscosimetric method yielded the following results (Table VIII). The viscosities were determined at 25° and 7°, the latter in the neighborhood of the freezing point for benzene.

TABLE VIII
Viscosity of Asphaltene solution in Benzene

	%	Time of flow in (sec.)	Spec. Grav.	k.M	M
@ 25°	0	25.1	.8765		
	4.102	45.75	.8852	.0646	1794
@ 7°	0	32.2	.8855		
	4.102	70	.8942	.08324	2312

The molecular weight obtained from the viscosity of the asphaltene solution in benzene at 25° compares favorably with the values given in Table VII. At lower temperature the asphaltenes associate but not to such an extent that molecular weights of 5-6000 can be expected.

Supersaturation

It has already been pointed out that asphaltenes in the dry state cannot be redispersed in the petrolenes. This is readily understood when the average size of the molecules forming the petrolenes are taken into consideration. The molecules are too large to penetrate into the interstices between the asphaltene molecules. The asphaltenes have been found to be soluble in the resins when a solution of both components in benzene is evaporated. However, from a benzene solution of asphaltenes and oily constituents from Mexican asphalt the asphaltenes will settle out after evaporation of the benzene has taken place. In some asphalts the oily constituents are of aromatic structure, and they would therefore keep the asphaltenes in solution under the above conditions.

Since the asphaltenes from the Mexican Asphalt are insoluble in their corresponding oily constituents, it can be said that the asphalt forms a supersaturated solution of asphaltenes.

P. von Weimarn¹⁰ who investigated the relation between particle size and supersaturation gave the following equation:

$$N = J P/L \quad (14)$$

where N = Dispersion coefficient—amount of particles for a given concentration; P = Degree of supersaturation influenced by the diffusion constant *i.e.*

¹⁰ Alexander's "Colloid Chemistry," 1 (1926).

molecular mass, and is a function of temperature; J = Factor expressed by the velocity of condensation of the solute. This factor varies in the same sense as the actual size of the particles in solution and the viscosity of the solvent. It is also a function of temperature; L = The ordinary solubility of the solute.

It follows that N is extremely great when colloid conditions result. This can be obtained by reduction of the solubility L by increasing P or increasing J .

From this formula it may be expected that the asphaltene particles are smaller when the asphaltenes are insoluble in their corresponding oily constituents.

Investigations made so far have shown that in asphalts which are very susceptible to temperature change, *i.e.*, when the viscosity coefficient increases rapidly with falling temperature, the oily constituents are composed mostly of aromatic hydrocarbons. Since the asphaltenes are soluble in these hydrocarbons, and thus are present in a lower degree of supersaturation, it can be assumed from von Weimarn's equation that the asphaltene particles are larger in size in the case of asphalts, which are less susceptible to temperature change. On the other hand, it may be predicted from their larger particle size that the relative viscosities of very susceptible asphalts are also higher. Unfortunately the work has not been carried through yet with different asphalts from different sources in the way previously outlined. However, the limited data on hand seems to confirm this viewpoint. For comparison the data may be given for an asphalt "A" of low susceptibility and an asphalt "B" of high susceptibility to temperature change both of the same asphaltene content (Table IX).

TABLE IX

	Asphalt "A"	Asphalt "B"		
Softening Point (Ring and Ball)	64.7°C	64.4°C		
Penetration 100 gr.				
5 sec. at 37.8°	100	47		
at 25°	41	16		
Asphaltene content	26.84%	26.97%		
Relative Visc. at 0°	1972	—*		
at 15.5°	1441	29360		
at 25°	544	9206		
at 37.8°	442	1889		
	k M	M	k M	M
k.M and M at 0°	0.1227	3400	—	—
at 15.5°	0.11768	3260	0.1656	4650
at 25°	0.10288	2850	0.1469	4080
at 37.8°	0.09857	2730	0.1214	3370

*This asphalt at 0°C behaved almost as a solid body, so that its viscosity was too great to be measured.

Since we have not yet determined the molecular weight of the asphaltenes from these two asphalts when in the monomeric state, we have to consider the

molecular weights in relation to this value at 37.8°C to bring these values to the same basis of comparison. The relations of the molecular weights are:

	Asphalt "A"	Asphalt "B"
@ 0°	1.24	—
@ 15.5°	1.19	1.38
@ 25°	1.04	1.21
@ 37.8°	1.00	1.00

The data seem to be in qualitative agreement with von Weimarn's equation.

Summary

Asphalts have been considered as a sol of asphaltenes in a mixture of asphaltic resins and oily constituents. Viscosity measurements have shown that asphalts have high relative viscosities at lower temperatures only, whereas, in the liquid state they behave like ideal solutions.

Structural viscosity has not been found to occur in the asphalts which have been investigated; it is probable, however, that structural viscosity is more pronounced with higher concentrations of asphaltenes.

An equation has been developed to calculate the molecular weight of the solute from viscosity measurements— $\log \text{ relative viscosity} = c.k.M.$ —where c denotes concentration in weight percent, k a constant, and M molecular weight.

The application of this equation, together with adsorption measurements of asphaltic resins on asphaltenes, seem to indicate that contrary to general opinion high relative viscosity is brought about by association rather than by solvation.

Von Weimarn's equation dealing with particle size and degree of supersaturation was found to hold qualitatively for asphalts from two different sources which have the same asphaltene content, but show differences with respect to susceptibility to temperature change.

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THE SORPTION OF ORGANIC VAPORS BY GLYPTAL RESINS

BY CLARENCE H. WINNING AND JOHN WARREN WILLIAMS

Within the last years considerable progress has been made with studies whose purpose is to elucidate the structure of organic compounds of high molecular weight. The formation of these substances is thought to result from a number of recurring atomic groups which are linked together into large units by primary valence forces. A number of these units may or may not then be associated into larger groups to form what are known as crystallites or micells. Gel substances of this general type exhibit what we understand as colloidal properties. A surprisingly large number of these substances show regularities in the association of chain molecules and of the micells, but others are characterized by the presence of giant molecules arranged with a high degree of randomness. The resin formed by the reaction between glycerol and phthalic acid, technically known as glyptal, seems to be one of the latter type. It is, nevertheless, a porous body, and as such should show a swelling under proper experimental conditions.

There are two general methods for the study of the swelling of a gel. In the first one, the substance is immersed in a liquid and the changes produced in certain of its physical properties are observed. For example, there will be a change in the volume, a change in the power to scatter light, and a change in the refractive index. The other method, commonly known as sorption, consists in allowing the porous body to come to equilibrium with proper vapors. The relationship between the two methods is obvious at the saturation pressure of the vapor.

The work to be reported in this article is a sorption balance study of the equilibrium of glyceryl phthalate resins in the presence of acetone and methyl alcohol vapors. Its objects are five-fold: 1. To determine the form of the sorption isotherms at several temperatures and to interpret the curves in terms of the porous structure of the resin. 2. To determine the heat of the sorption process by the comparison of two isotherms. 3. To make an estimate of the average pore size from the sorption behavior in the neighborhood of saturation. 4. To study the changes in structure produced by variations in the curing process to which the resin has been subjected. 5. To study the reversibility of the sorption process.

So little is known regarding the structure of a synthetic resin that several kinds of investigation likely to contribute to the ultimate interpretation should be made. Experiments of the type to be reported here at least make possible a basis for the scientific comparison of different resins. It is also believed that when sufficient data can be accumulated the method will be successful in demonstrating the existence and type of micellar structure. To obtain an estimate of the dimensions of these micells it will probably be neces-

sary to combine these results with deductions from other even more physical lines of reasoning such as a study of the elastic properties of the gel and the dielectric constant relations of proper suspensions in liquid media. Data of this sort should be of considerable value to industries interested in the development of these and other substances as plastics and varnishes, because among other things they will contribute to an understanding of such properties as the rigidity of the resins, and the retention of vapors by them.

Experimental

Apparatus and Procedure. The experimental results to be presented are sorption and desorption isotherms of glyptal resins in equilibrium with different vapor pressures of acetone and methyl alcohol.

The apparatus used was a McBain-Bakr balance,¹ adapted to the sorption of vapors by powdered resins. In principle it is a spring balance suspended in an evacuated chamber. The required vapor pressure of the organic liquid was obtained by maintaining a known temperature in a bath surrounding the liquid which had been collected in the reservoir, which is in turn connected to the sorption chamber proper. The amount of sorption at any vapor pressure was obtained from the difference in weight, determined from the elongation of the spiral, between the sample before and after the sorption process had taken place.

The procedure will be evident from a study of Fig. A, in which the apparatus is diagrammed. The four quartz springs were suspended from brass cylinders which were mounted in the special sorption chambers. The ground glass joints fitted with mercury seals facilitated the changing of samples. The chambers containing the springs were maintained in a well-insulated air thermostat fitted with double plate glass windows on opposite sides. The temperature in the bath was controlled by a special mercury-toluene regulator which permitted variations not greater than 0.2°C.

Evacuation of the system was accomplished by means of a mercury vapor condensation pump backed by an oil pump of conventional design. Oil vapors were prevented from entering the vacuum line and organic vapors were prevented from reaching the pump by means of liquid air traps. The pressures were indicated by a McLeod gauge.

After thorough evacuation of the system to remove moisture the liquid whose vapors are to be sorbed is introduced into a side tube J—connected with the main sorption chamber by a capillary tube. The liquid was then frozen with liquid air and the system again evacuated. As the solidified liquid was allowed to warm up and melt, any gases which had been dissolved were given up. The liquid was again frozen and the system re-evacuated. This process of outgassing the liquid and evacuation was repeated until the dissolved gases had been completely removed.

The lengths of the quartz springs were then measured to obtain the weight of the dry resin samples in vacuo. These samples are contained in extremely

¹ J. Am. Chem. Soc., **48**, 690 (1926).

thin glass bulbs fitted with hooks to attach them to the spirals. Each balance had been previously calibrated throughout the working range by noting the elongations caused by known weights, using a precision cathetometer which was accurate to 0.01 mm. Within the limits of error and within the range in which we were operating the elongations produced over successive 0.05 g. intervals could be considered to be proportional to the weights attached. Previous to the calibration the springs had been carefully annealed.

The liquid was then distilled at a low vapor pressure from the side tube through the capillary tubes connecting tubes *I* into the bottoms of the liquid retaining tubes *H*. Condensation on and sorption by the samples was pre-

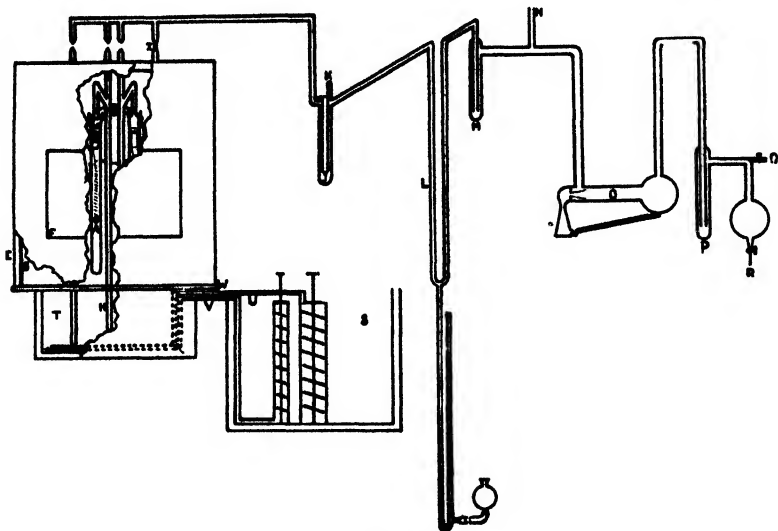


FIG. A
Diagram of Apparatus

vented by chilling the bottom of these tubes with liquid air contained in vacuum bottles. After a sufficient amount of the organic vapor has been condensed each of the four units is sealed off at the constricted connecting tube.

To control the vapor pressure of the liquid in the sorption chambers it was necessary to circulate a liquid at controlled temperatures about the portion of the tubes in which the liquid was contained. Since it was at times necessary to cool the liquid to temperatures below zero it was convenient to use a mixture of glycerine and water for this purpose. It was pumped from a thermostat in which the temperature was regulated to 0.02° C. The circulation was such that at least 6 liters of the thermostat liquid flowed in each direction in 1 minute. The corresponding vapor pressure of the sorbate was obtained from standard tables of physical constants. Measurements of the elongation of the spiral were always continued until no change in the reading of the cathetometer could be observed after a 4 hour period. It was then assumed that the sample had reached a constant weight. That this assumption was not always entirely justified will be evident from a study of the sorption curves in the regions of

low vapor pressure. It happens, however, that the very slow rate of sorption in these cases is of considerable importance for the conclusions with regard to the structure of the resin, and they will be considered in some detail. Constant weight was never attained in less than 24 hours, and sometimes considerably longer periods of time were required. The amount of sorption at any of the pressures used could always be calculated from the weight of the dry sample in vacuum. For each sample at a given temperature both sorption and desorption curves were obtained. The pressures ranged from very small values to values approaching saturation. This method of experimentation has the advantage that in addition to the equilibrium value itself the rate at which the sorption equilibrium is attained may be observed.

The sorption took place in samples of resin which had been prepared in powdered form. The adsorption on the external surface of the powder was of minor importance compared to the process taking place within the structure of the resin itself.

Materials used. The acetone was purified by distillation from the sodium iodide addition product, and subsequent drying, following the directions given by Shipsey and Werner.²

Methyl alcohol of a high grade of purity was subjected to the treatment described by Bjerrum and Zechmeister³ for the removal of water.

The glyptal resin samples were prepared using glycerol (98% grade) and phthalic anhydride (C.P. grade). The relative proportions of these substances used was two molecules of glycerol to three molecules of phthalic anhydride. The glycerol was first heated to 200° C, then the anhydride was added, taking care to always maintain this temperature during the course of the reaction. The reacting mixture was frequently stirred. The heating was continued for exactly four hours. Samples of this resin were cured in an oven maintained at 105° C for periods of time up to 275 hours. All resin samples, unless otherwise noted, were taken from the same parent resin and cured for the lengths of time indicated in the tables of data, and in the discussion of the solubility of the resins.

A cellulose acetate sample was obtained from the Eastman Kodak Company. It was described by them as having been prepared by a method which "leads to the complete solution of the cellulose acetate in the esterifying bath."

Data and Results

Data and Graphs for the Sorption Isotherms. The experimental data are presented in the form of tables and graphs. In each case the number assigned to the graph corresponds to the number of the table. The data of Table I have been plotted on three curves. The first graph shows the position of the sorption and desorption isotherms at 50° for acetone vapor on the several samples of glyptal resin. Recognizing the fact that the sorption and desorption processes were so slow in the region of the very low relative pressures that it would be quite impossible in the time at our disposal to attain the true

² J. Chem. Soc., 103, 1255 (1913).

³ Ber., 56, 894 (1923).

equilibrium positions of the isotherms, we have plotted a second series of isotherms which have been called equilibrium curves. These curves have been obtained by an averaging process from the sorption and desorption curves as actually observed. In assigning an x/m value for a given p_x/p_s the relative rates of the sorption and desorption processes have been considered. For the more nearly reversible systems (the cured resins) the greater portion of the equilibrium curve could be calculated without much difficulty, and, we believe, with considerable accuracy. It is of course true that there is a considerable uncertainty in the position of the equilibrium isotherms at the very low relative pressures. It may be well to remark at this point that what conclusions we have drawn from the first portions of the various isotherms in the sections of this report have depended not upon the position of an equilibrium curve but upon the rate at which progress toward such an equilibrium was being made. These equilibrium curves are shown in Fig. 1a.

Fig. 1b, for which data are found in Table I as well as in Table Ib, shows the 35° and 50° isotherms for acetone vapor being taken up by the sample of cellulose acetate. It will be observed that the hysteresis is somewhat less at the higher temperature. The points on the curves have been obtained only after at least 24 hours was allowed for the attainment of equilibrium. Even under these conditions there was some evidence that the true equilibrium position had not been attained, in spite of the fact that several recent investigators claim that other vapors come to equilibrium with this and similar material in periods of one and two hours. We should also mention that all of our experiments have been made in a continuous manner, the relative saturation

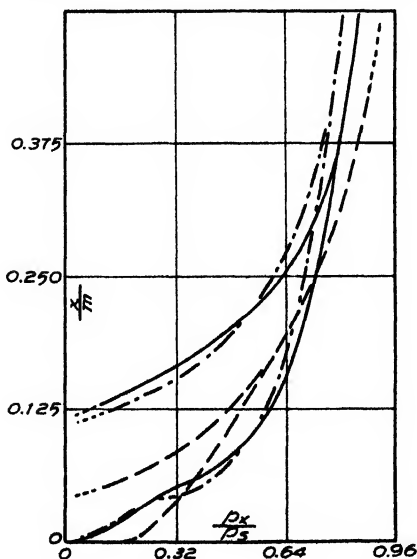


FIG. 1

Acetone— 50° Isotherms
 — — — Special Resin
 — — — Resin I
 - - - Resin II
 . . . Resin III

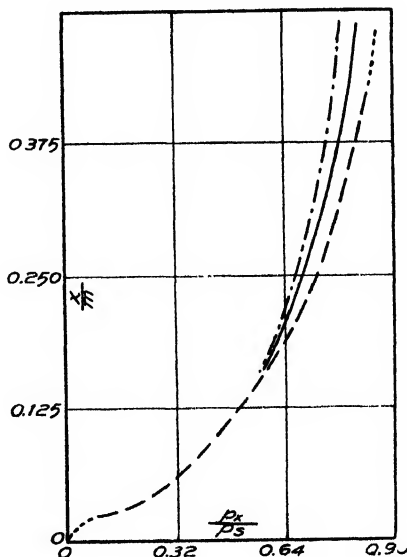


FIG. 1a

Acetone— 50° Isotherms
 Equilibrium Curves

tion pressures being gradually increased, and, after reaching a practical limiting value, they were gradually reduced, with stops of not less than 24 hours at pressures where observations were made.

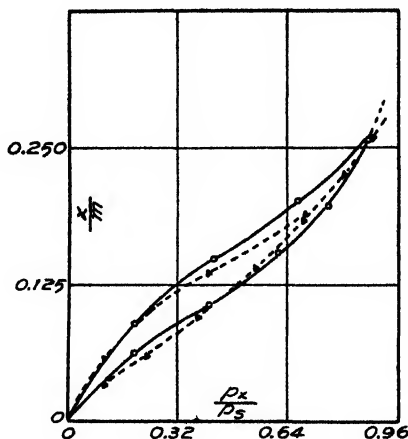


FIG. 1b
Acetone—Isotherms for Cellulose Acetate
----- 50° Curve
——— 35° Curve

TABLE I
Data for 50° Isotherms—Acetone Vapor

p_x/p_s	Amount sorbed per Gram (x/m)				Cellulose Acetate
	Resin I*	Special Resin**	Resin III		
0.109	0.011	0.011	0.000		0.035
.230	.033	.034	.007		.060
.374	.059	.043	.057		.096
.543	.097	.101	.141		.141
.687	.206	.236	.215		.185
.804	.378	.465	.308		.228
.882	.560	.670	.408		.261
.687	.273	.304	.222		.190
.408	.185	.173	.102		.136
.109	.130	.120	.050		.057

* In this and the following tables, as well as in the text, Resin I refers to a sample of glyptal resin prepared by cooking for exactly 4 hours, which is uncured; Resin II refers to samples of the same resin which have been cured for 42 hours; and Resin III refers to similar samples which have been cured for 275 hours.

** This resin differs from Resin I in that it was removed from the reaction flask at the end of a 3 hour period.

TABLE Ib

Data for 35° Isotherms—Acetone Vapor

Cellulose Acetate			
p_x/p_s	x/m	p_x/p_s	x/m
0.193	0.063	0.871	0.258
.407	.106	.662	.201
.608	.155	.424	.149
.752	.197	.193	.090

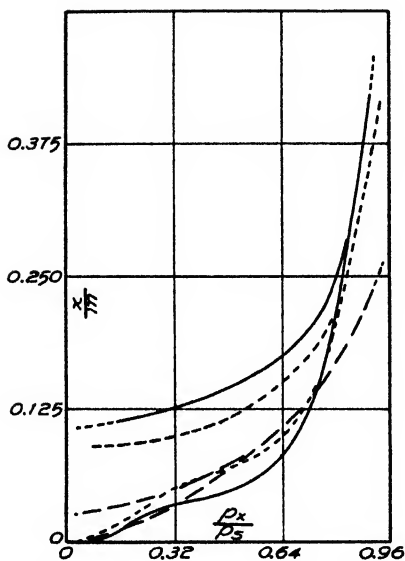


FIG. 2

Methyl Alcohol—50° Isotherms

— Resin I
 - - - Resin II
 — · — Resin III

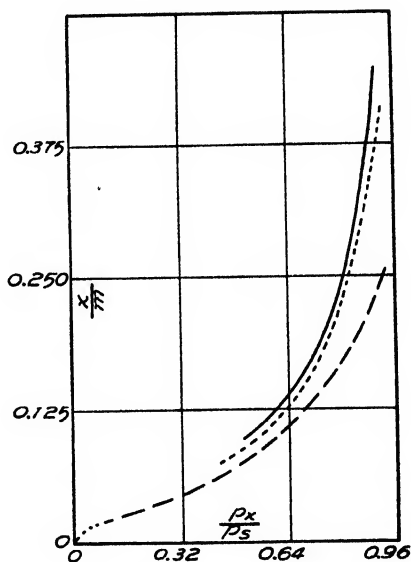


FIG. 2a

Methyl Alcohol—50° Isotherms
Equilibrium Curves

Table II and Figs. 2 and 2a have been constructed from the experimental data taken during the 50° sorption and desorption process for resins in the presence of methyl alcohol vapor. The figures correspond to those just presented for the behavior of the resins in the presence of acetone vapor.

In order to be able to compare directly the difference in behavior between acetone and methyl alcohol with respect to a given resin Table III and Fig. 3 have been presented. They show that although the affinity of the resin for acetone is greater than it is for methyl alcohol, the rate at which the methyl alcohol is able to penetrate the resin at the beginning of the sorption process is the greater.

TABLE II

Data for 50° Isotherms—Methyl Alcohol Vapor
Amount sorbed per Gram (x/m)

p_x/p_s	Resin I	Resin II	Resin III	Cellulose Acetate
0.073	0.002	0.005	0.007	0.014
.265	.031	.041	.026	.038
.456	.044	.067	.062	.060
.748	.148	.155	.143	.102
.898	.408	.344	.228	.134
.762	.220	.195	.149	.120
.476	.146	.116	.072	.079
.167	.115
.073093	.029	.014

TABLE III

Data for 35° Isotherm
Methyl Alcohol Vapor
Resin II

p_x/p_s	x/m
0.147	0.010
.355	.035
.559	.081
.760	.124
.910	.252
.708	.174
{ .430	.132 }
{ .430	.087 }

Data for 35° Isotherm
Acetone Vapor
Resin II

p_x/p_s	x/m
0.193	0.005
.288	.016
.425	.071
.582	.130
.794	.338
.648	.238
.467	.195
.256	.183

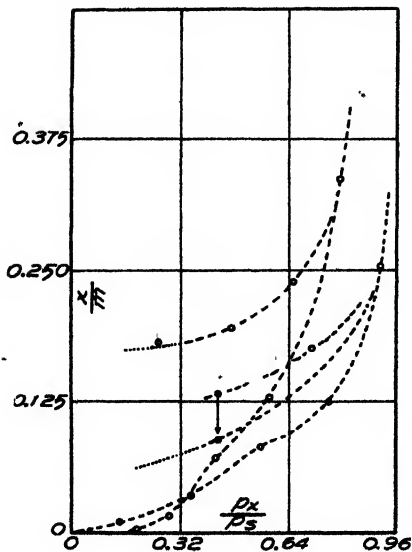


FIG. 3
Resin II—35° Isotherms
Upper Curve—Acetone
Lower Curve—Methyl Alcohol

The data of the three tables represent approximately one-half of the experimental measurements. The other data, obtained for the most part at 35°, are in all respects similar in character, and have not been published solely in the interest of a saving in space.

Solubility of the Resins in Acetone and Methyl Alcohol. Approximately 0.1 g samples of each of the series of resins were covered in test tubes with 5 to 6 cc of dry solvent. The tubes were then sealed. The solvent action was followed for a considerable period of time. The tubes were viewed by both transmitted and reflected light, and in a Tyndall beam. The results of these solubility tests, using acetone and methyl alcohol as solvents, are tabulated below. The word "solution" is

used in the sense in which it is usually applied to materials of this sort. The resins used were of the series previously described in the section on the purification and preparation of materials.

Acetone as Solvent

Resin cooked 3 hours.—Immediately soluble to give a clear liquid. Shows faint Tyndall beam.

Resin cooked 4 hours (Resin I).—Immediately soluble to give a clear liquid. Shows Tyndall beam.

Resin II. (Resin I cured 42 hours).—Apparently insoluble. Liquid gives Tyndall beam. Solutions appear clear to ordinary observation. Insoluble gummy residue.

Resin III. (Resin I cured 275 hours).—Very faint Tyndall beam. Residue in powdered form.

Cellulose acetate.—Gives clear solution that exhibits Tyndall beam.

Methyl Alcohol as Solvent

Resin cooked $3/4$ hour.—Dissolves in a few hours. Solution is slightly cloudy. Cloudiness later disappears and a slight precipitation is visible on the walls of the tube. Very faint Tyndall beam.

Resin cooked $2\frac{1}{2}$ hours.—Partly dispersed in solution to give cloudy suspension, which later settles out on walls of tube. Very faint Tyndall beam. Insoluble portion at bottom is transparent gummy mass.

Resin cooked 3 hours.—Slight Tyndall beam. Solution appears clear to ordinary observation. Less sedimentation on walls than for previous resins. A transparent residue of insoluble resin remains.

Resin I.—Gives clear solution which shows slight Tyndall effect. There is also transparent and insoluble residue left in the bottom of the tube.

Resin II.—Gives clear solution which shows faint Tyndall effect. Transparent and gummy residue remains.

Resin III.—Gives a clear liquid which shows no Tyndall effect. Residue appears as it did when dry.

Cellulose Acetate.—Gives no evidence of solubility.

The condition of the samples in the various tubes containing acetone and methyl alcohol after they had been kept in an oven at 105° was apparently unchanged after one week.

These data show that acetone is a much better solvent for the resins than methyl alcohol.

Discussion of Results

The sorption of vapors by gels of the swelling or elastic type and the resultant volume change has been the subject of many investigations. The amount of vapor which may be taken up by them and the degree and manner in which they swell are undoubtedly related to their chemical and physical structures, yet data of the type presented above without other evidence probably can never give a completely satisfactory means to describe them. It is well known that different gels swell to varying degrees up to the extreme case where a kind of solution of the solid body is effected through resolution into the constituent

micells or other structural units. Where such a solution has been formed it seems clear that a sorption process is no longer involved, but in the intermediate cases it is not readily possible to say where one process has been completed and the other has begun. But even in spite of such difficulties one can readily justify sorption studies on substances of the sort considered here in terms of the information which is made available by them.

A number of theories have been proposed to describe the structure of resins as highly polymerized organic substances. For purposes of discussion we shall classify them as gels, since it is more or less tacitly agreed that they are heterogeneous in the sense that there is present both a continuous and a disperse phase, with the two phases forming a network. The structure of highly polymerized organic substances is usually interpreted on the assumption that the disperse phase is made up of simple molecular units which have aggregated to form micells. In some cases these micells are now known to be arranged according to a regular pattern while in others it is supposed that the arrangement is a random one. In the case of the glyptal resins the existence of building units of the micellar type has not, as far as we are aware, been demonstrated. Also in some ways it does not seem logical to assume their existence, rather it is advantageous to consider the most important structural units to be giant molecules. It is of course true that these giant molecules may associate with each other in a way which is similar to the dipole association of liquids like water and alcohol, forming units which might be compared to micells, but they will be the result of chance aggregations and will not result in any regular arrangements.

One may even go so far as to predict that when molecular size and molecular weight determinations with any particular sample of glyptal resin can be made the units will be found to be monodisperse, a result similar to that which has already been found by Svedberg and his associates for a number of the proteins. To start the resin formation 1 molecule of glycerol may be assumed to react with 3 dibasic acid molecules. This substance may then combine with 3 more glycerol molecules and the process might be considered to be an endless one, with the chains becoming more and more branched as new glycerol molecules take part in the reaction. But the results of recent molecular structure studies teach that there is a certain freedom of rotation of groups about single valence bonds and that the angles made by the valence bonds attached to the carbon and oxygen atoms remain sensibly constant in compounds. Therefore it may be expected that the reaction will eventually be retarded due to inner esterifications leading to the formation of closed rings.

The sorption of vapors by such a system will be a slow process because the molecules of the sorbate will have to penetrate between and around the giant molecules. This process should therefore depend to a large extent upon the size and polarity of the vapor molecules. The strong cohesive forces holding the larger units to form the solid material will have to be overcome so that there must be an actual attraction between sorbent and sorbate for the permeation of the solid mass. Then the structure will be progressively opened up through the continuation of this process which results in the attachment of

solvent molecules over the surface of the structural units. The complete solution of the resin may be accomplished in the case of certain liquids through the complete resolution of the solid into these constituent units. It seems likely that in such cases a considerable amount of liquid will be held by capillary forces in the regions between the giant molecules which have now been released from any elastic strain. The vapor molecules will be increasingly sorbed as their relative pressures become higher and higher.

Form of Sorption Isotherms. The equilibrium sorption isotherms of swelling gels are typically "S" shaped. The sorption isotherms for cellulose acetate which we have determined show this behavior very nicely but our isotherms for the glyptal resins do not entirely conform. We are confident that the reason for this condition is due to our failure to realize the true equilibrium at the very low relative vapor pressures, rather than to any failure of the resin to conform to the general behavior. The form of our sorption isotherm is shown by the full line of Fig. 4. There has also been indicated by broken line the probable equilibrium position of the isotherm. The structure of the resin is so extremely fine that such gases as hydrogen and oxygen pass through thin films only with the greatest difficulty. The penetration by larger molecules such as methyl alcohol and acetone vapors will therefore be very slow even in the evacuated sorption chamber and true equilibrium can be attained only after very long periods of time.

For purposes of discussion the typical isotherm will be divided into three regions. In the first of these regions it may be said that the giant molecules are held together by strong cohesive forces which are eventually overcome by the highly polar sorbate molecules. An inspection of the experimental data, and a study of the rate at which the vapors are sorbed show that these cohesive forces have increased in strength as the curing time of the resin is increased. At the same time the sorption tendency or adhesional affinity is correspondingly decreased. The sorption and desorption curves may not coincide, because the reaggregation process is not a reversible one, but it seems more probable that the true equilibrium conditions have not been attained.

Once the sorbate molecules have penetrated the structure of the resin the equilibrium value for the amount adsorbed is attained much more readily. This is indicated by the change in the slope of the isotherm in passing from the first region to the second one. It seems probable that by the time the relative

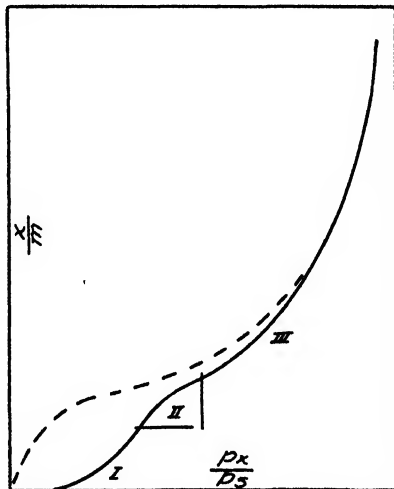


FIG. 4

Schematic Diagram of Sorption Curve
 ————— Observed Curve
 - - - - - Equilibrium Curve

vapor pressures corresponding to the second region have been reached a film of definite thickness has been formed between all giant molecules, and about the branches and rings of these units, in spite of the fact that the sorption and desorption curves are not entirely reversible. The region in which the isotherm becomes parallel to the pressure axis corresponds to the completion of the process which began in region I.

As the external vapor pressure is increased to values corresponding to the beginning of the last region it seems logical to assume that the giant molecules become separated to such an extent that the voids become inter-connecting to form capillaries. The liquid will be condensed in these capillaries and held there at a reduced vapor pressure because of the curvature at the surface. As the sorption continues these capillary spaces fill up and at the same time extend in dimension. The resin takes up considerable quantities of either acetone or methyl alcohol until the saturation value at a given relative pressure is reached, this process being a reversible one practically throughout this third region. It does depend somewhat upon the treatment to which the resin has been subjected in its preparation. This indicates that the gel returns to the same packed condition as the vapors are removed from the capillaries which have been formed in the swelling process.

Thermodynamics of the Process. The results of the experiments are thus explained by assuming a model in which giant molecules are the structural units and in which the process of adsorption (Regions I and II) is followed by one of condensation (Region III). A consideration of the thermodynamics of the process provides ample justification for the division into adsorption regions and a condensation region. If, as has been done in the introduction, it is possible to compare the sorption of vapors with the process of wetting, it can be shown that when one mol of the liquid sorbate, of molecular weight M , is transferred isothermally to the adsorbent which has already adsorbed x/M mols per g, the free energy change in the process is given by the expression

$$-\Delta F = RT \ln p_s/p_x$$

where $-\Delta F$ is the free energy change when the amount x is adsorbed, p_x is the equilibrium pressure above the sorbent when the amount x is adsorbed, p_s is the saturation pressure, R is the gas constant, and T is the absolute temperature. Using the data of an equilibrium isotherm and this expression there can be calculated the change in free energy as the amount adsorbed, x , is increased. As would be expected the values are highest at the beginning of the process, but as the relative saturation pressures increase the values become smaller and smaller.

Values for the decrease in free energy of the 50° and 35° sorption of acetone vapors on the resin sample which had been cured 275 hours are given in Table IV. In the first and second columns there are tabulated observed and equilibrium values of x/m for corresponding values of the relative saturation pressures, p_x/p_s . These data are chosen as typical.

TABLE IV
Free Energy of Sorption Process

50° Isotherm x/m Ads.	Acetone Vapor x/m Equil.	p_x/p_s	Resin III - ΔF Cal.
0.000	0.025	.1	1478.
.002	.034	.2	1033.
.029	.054	.3	774.
.067	.085	.4	585.
.115	.125	.5	446.
.168	.168	.6	328.
.227	.225	.7	230.
.309	.308	.8	146.
.448	.448	.9	67.

35° Isotherm	Acetone Vapor		Resin III
0.000	0.047	.1	1409.
.000	.051	.2	984.
.005	.064	.3	737.
.032	.085	.4	561.
.092	.120	.5	424.
.165	.165	.6	312.
.217	.216	.7	219.
.320	.327	.8	136.

The change in heat content for the process, $-\Delta H$, may be obtained from the free energy change and its temperature coefficient, using the Gibbs-Helmholtz equation.

$$\begin{aligned}\Delta H &= \Delta F - T \left(\frac{\partial \Delta F}{\partial T} \right)_p \\ &= RT^2 \frac{\partial \ln p_x}{\partial T} - RT^2 \frac{\partial \ln p_s}{\partial T}\end{aligned}$$

The first term on the right side of this equation will be recognized as the differential heat of adsorption, while the second term, which is quite independent of the amount adsorbed, is the molal heat of vaporization of the liquid being adsorbed. This equation may be written in integrated form for use as follows:

$$-\Delta H = \frac{2.3 R T_1 T_2}{T_2 - T_1} \left(\log \frac{p_{x_2}}{p_{x_1}} - \log \frac{p_{s_2}}{p_{s_1}} \right)$$

Having determined the equilibrium positions of two isotherms (35° and 50°) it is possible to calculate the differential heats of adsorption for the several systems studied as the amount of vapor adsorbed is increased. It is found in every case that this quantity decreases to a value which becomes constant as the amount of vapor adsorbed reaches the value which marks the beginning of the third and last sorption region. Further, this value is constant for the

glyptal resins which have been given different treatments in preparation as long as a single kind of sorbate molecule is involved, and is, within the limits of experimental error, equal to the molal heat of vaporization of that substance. In other words the adsorption has been completed when the third region of the process is reached and it is followed by a condensation in the capillaries which have been formed by the uncoupling of the residual valence forces which held the structural units together. Typical results of calculations for the differential heats of sorption are given in Table V.

TABLE V
Differential Heats of Sorption

Resin III Equilibrium Pressures		x/m	Acetone Vapor Heat of Sorption per Gram Mol of Acetone
35°	50°		
41.6 m.m.	159.3 m.m.	0.045	305. cal.
62.3	173.3	0.050	322.
102.5	200.9	0.062	153.
123.3	225.4	0.075	137.
153.8	269.5	0.100	127.
176.7	306.3	0.125	125.
213.4	374.9	0.175	128.
240.4	428.8	0.225	131.
262.6	469.3	0.275	132.
276.1	499.9	0.325	135.
291.0	524.4	0.375	134.
302.8	544.0	0.425	133.

Resin III		Methyl Alcohol Vapor	
109.0	202.0	0.075	254. *
127.0	245.0	0.100	270.
141.0	279.5	0.125	280.
153.0	304.0	0.150	282.
171.0	343.0	0.200	286.
184.0	370.0	0.250	287.
192.3	385.5	0.287	286.

* The values at the lower relative saturation pressures are in error due to greater difficulty in properly locating the equilibrium isotherms for methyl alcohol for which fewer data are available.

The molal latent heats of vaporization for the two liquids have been calculated from the vapor pressure data. At corresponding temperatures the values are approximately 130 calories and 285 calories, respectively. *

Estimation of Pore Size. One of the primary objects of this research was to make information available concerning the porosity of these resins. Sorp-

* Sheppard and Newsome (J. Phys. Chem., 36, 930 (1932)) have recently treated data for the sorption of water vapor by cellulose acetate films in a similar manner.

tion studies seem always to receive consideration for such a task, the reason being that in certain quarters it is believed that all material sorbed by a porous body is liquid condensed in its capillaries. Although we do not care to defend this viewpoint, we do feel that the application of the Kelvin relation between capillarity and vapor pressure to our data will permit an estimation of the size of the intermolecular capillaries, especially in the regions of the higher relative pressures. The results of our calculations are intended to indicate an order of magnitude rather than an exact value. From the discussion given above we should have to conclude that the capillary process ceases to be operative for the smaller vapor pressures, so that the smaller values are probably considerably in error.

The Kelvin equation is

$$RT \ln \frac{p_s}{p_x} = \frac{2\sigma}{r} \cdot \frac{M}{d}$$

$$\text{or } r = \frac{2\sigma M}{dRT \ln p_s/p_x},$$

where p_s is the vapor pressure above a plane surface, p_x is the vapor pressure above the meniscus, σ is the surface tension of the liquid being condensed, M is its molecular weight, d is its density and r is the radius of the capillaries, which are considered to be cylindrical.

Using the data for the 35° isotherms for acetone being sorbed by the several samples of glyptal resin, the following results are obtained. It is assumed that the process of capillary condensation begins where $p_x/p_s = 0.1$. The data for the tables are taken from the extrapolated equilibrium curves.

TABLE VI
Values for Radius of Capillaries (Acetone)

p_x/p_s	$r \times 10^8$ cm.	Special Resin* x/m	Resin I x/m	Resin III x/m
.1	5.	—	—	.025
.44	14.	—	—	.100
.56	20.	.158	.154	.150
.72	35.	.312	.280	.237
.80	50.	.450	.375	.307
.84	66.	—	.437	.353

* This resin differs from Resin I in that the 200° reaction between glycerol and phthalic acid was stopped at the end of a 3-hour, instead of 4-hour period.

In the following table a corresponding set of data and calculated quantities are tabulated for a series of resins, the sorbate being methyl alcohol.

TABLE VII
Values for Radius of Capillaries (Methyl Alcohol)

p^*/p_s	$r \times 10^8 \text{ cm.}$	Resin I x/m	Resin II x/m	Resin III x/m
.1	3.	—	—	.017
.44	8.	—	.075	.062
.56	11.	.112	.100	.087
.72	19.	.176	.162	.135
.80	27.	.237	.220	.170
.88	36.	.370	.322	.214

These values are typical of the results obtained either with acetone or with methyl alcohol. The use of the Kelvin equation can be justified if each molecule of the condensed liquid is surrounded by like molecules, without the sphere of influence of the molecules forming the capillary walls. It is evident, then, that values as small as 3×10^{-8} cm for the effective radii can be of little significance because the molecules of the sorbed material would then have to be in contact with the solid sorbent. The values corresponding to higher x/m values are of what seems to be a proper order of magnitude.

Inspection of these tables seems to indicate that the structural units of the resin become larger as the curing process is continued. For a given relative saturation pressure, and therefore for a given capillary radius, the amount of vapor which is condensed decreases as the length of the curing process is increased. To explain this it seems necessary to assume that the number of these capillaries is greater for the less mature resins, which would indicate the presence of a larger number of smaller molecules. A study of the mechanical properties of the resin suggests that the increase in the size of the giant molecules is probably a lengthening of the irregular chains. This point will be discussed further in the next section where the effect of the curing process over the whole range of the sorption is considered.

Effect of Curing Process. The formation of a glyptal resin may be thought of as occurring in several stages of which we shall mention but two. The first is the rather high temperature reaction between glycerol and phthalic acid in which water is eliminated. If the reaction has been stopped at the proper time a hard, brittle substance is formed on cooling. A second stage of the reaction is the curing process in which this hard brittle substance is heated to approximately 105° over extended periods of time. Although practically no more water is now eliminated the resin undergoes a very pronounced change, because after from 10 to 14 days at this temperature it has become extremely tough and more resistant to solvents. In this condition it will withstand sudden shocks and may be machined quite readily. It seemed of interest to compare the relative abilities of the cured and uncured resins to take up and give off organic vapors to see if any differences in behavior might be interpretable in terms of the respective structures.

The relative positions of the several sorption isotherms indicates that as the curing process is continued the structure becomes more firmly knit together.

The uncured resin takes up the vapors more readily than either of the cured resins. Its isotherm rises quite sharply at the beginning of the sorption while the amounts of vapor taken up by the cured resins are exceedingly small over the same pressure range. The filming process or saturation of the structural units is completed at relatively lower vapor pressures in the case of the more immature resins. Since in these portions of the isotherms the natural cohesive forces holding the resin together must be overcome by the mutual attraction between sorbent and sorbate it is evident that it is becoming more and more difficult for the sorbate molecules to penetrate. The rather large differences in the sorption isotherms for the various resins in the lower parts of the curve show that the physical and chemical structure is profoundly changed by the curing process.

In the second region of the sorption curves, the amount adsorbed at the "saturation value" varies with the particular resin sample. The exact significance of this variation is difficult to determine, because it occurs in a region which is intermediate between two others where the processes of sorption are distinctly different. The former region is characterized by a process probably more chemical in nature, while the latter region is characterized by a process undoubtedly more physical in nature. The definite appearance of an intermediate region in the sorption isotherms must depend upon the fact that this region represents the first real approach to equilibrium in the sorption process. After the process taking place in this region is completed, the resin molecules are considered to be separated by a film of sorbate molecules, so that any available spaces between the closely packed giant molecules now have become interconnecting.

At this point there is a sharp rise in the sorption curve, the beginning of our third region. The point of inflection in the curve is quite pronounced. For the less mature resins this point of inflection is reached at lower vapor pressures. This may be interpreted to mean that the process of capillary condensation begins at lower vapor pressures for these less mature resins, because a greater number of smaller interconnecting capillaries have been formed, making it possible for larger amounts of the condensed vapors to be held at the lower relative pressures. We may conclude that the less mature resins have smaller structural units, for such a structural system would furnish a larger volume of small capillary spaces. A greater number of the smaller capillaries also accounts for the greater steepness of the sorption isotherms for the less mature resins.

This conclusion appears to be justified by a consideration of the solubilities of the different resins as prepared by us. The uncured and less mature resins are more soluble in any solvent. Since swelling may be considered essential to the gel dissolution process, we may reasonably expect that the capillary condensation as it proceeds is a process that separates and disperses the resin molecules. The degree of dissolution appears to be related to the steepness of the isotherms in the final stages of the sorption process.

A comparison of the isotherms for a series of resins at 35° and 50° for either vapor, and a consideration of the previous table of pore sizes lead us to

conclude that the smaller capillary spaces of the less mature resins are capable of holding a larger quantity of liquid than are the sum total of small and large capillary active spaces of the more mature resins. For the latter resins it is possible to obtain much more accurate values for x/m as we approach the saturation value. Thus the matured resins have a greater tendency to retain some of their original structure that holds the mass firmly together, and complete dissolution by a capillary condensation process is impossible.

Reversibility of the Sorption Process. As sorbed liquid is withdrawn from an elastic gel, the gel molecules again approach each other to give a more closely packed structure. This behavior distinguishes swelling gels from non-swelling gels. If the vapor pressure of the sorbed liquid is decreased to a negligibly small value, all sorbed vapors are eventually removable, and the gel returns to its original structure and volume. This behavior of swelling gels has been typical of the gel systems previously studied, and is also undoubtedly typical of the gel system investigated in this research. On the whole the swelling gels could be classified as dried out gels, for they were originally deposited from a solution of some kind. It is quite natural to assume that such gels after swelling in a given liquid would return to their original structure and volume. In this research a gel of vitreous nature has been studied in its behavior as a swelling gel, with acetone and methyl alcohol vapors as sorbates. A complete desorption of vapors has not been effected in any case because of the time which would be required, but an inspection of the series of sorption and desorption isotherms and of the assumed equilibrium curves for more mature resins reveals that a considerable portion of the curve is reversible. Actually, and for practical purposes it may be said that the last traces of vapor, taken up in the region of low relative saturation pressures, are held so tenaciously that we could not, in any such experiment as performed here, expect to attain complete desorption. The blushing of varnishes has been attributed to such a retention of certain solvents which take on moisture from the atmosphere when the humidity is exceptionally high.

Rate of Sorption and Desorption. In studies of the sorption of water by wood Pidgeon and Maass⁴ found that their final equilibrium was generally reached from the dry state in under half an hour in the case of moderate vapor pressures, while the corresponding desorption process required several hours. Polanyi and Welke⁵ found that periods even up to 2 and 3 days were necessary for the attainment of equilibrium for the adsorption of gases on charcoals. In the case of the glyptal resins it was found that relatively long periods of time (at least 24 hours) were required for the sorption process and that even much greater periods were required for the desorption. Equilibrium was always most difficult of attainment in the region of low vapor pressures. There are given below two graphs (Figs. 5 and 6) which have been prepared to indicate the rapidity with which the sorption and desorption processes come to equilibrium.

⁴ J. Am. Chem. Soc., 52, 1053 (1930).

⁵ Z. physik. Chem., 132, 371 (1928).

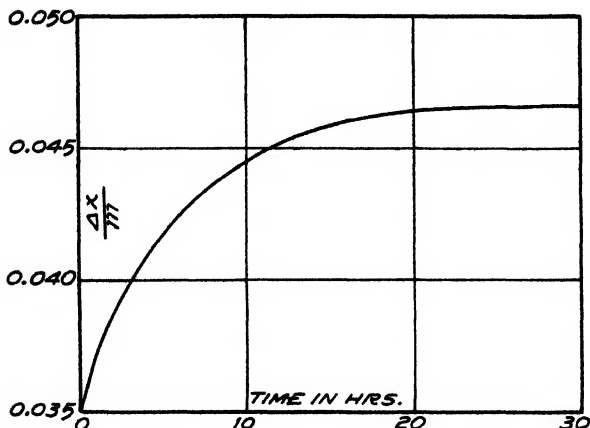


FIG. 5

Sorption—Time Curve
Acetone—50° Sorption on Cellulose Acetate
Change in p_x/p_s 0.109 to 0.230

It is believed that our data are sufficient to justify our method for determining the position of what we call the true sorption isotherms. The only real difficulty in coming to an equilibrium was found in the region of low relative pressures. In the condensation region the sorption and desorption curves were reasonably reversible. The positions of equilibrium could also be determined with some accuracy in the region of the transition from adsorption to condensation. The more mature resins always gave better reproducibility, probably due to a greater rigidity of structure and larger size of capillary.

Thus, any hysteresis which our data and curves indicate is to be found in the region of low relative saturation pressures, and is probably to be explained on the basis of a closely knit structure that is only slowly permeated by gases and vapors. It has been noted that the most mature resins with their greater rigidity of structure show the least hysteresis. In the hysteresis region it

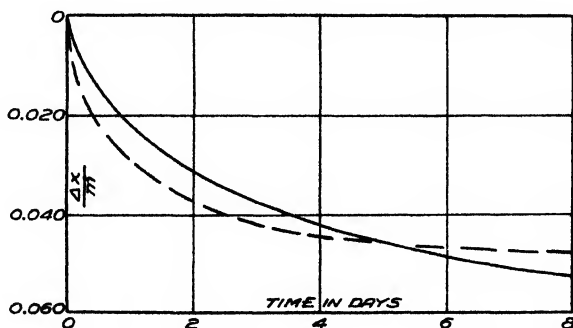


FIG. 6

Desorption—Time Curve
Acetone—50° Desorption
——— Resin I
----- Resin III
Change in p_x/p_s 0.613 to 0.011

seems likely that associated structural units have become separated with the breaking of secondary valence bonds, and molecules of either acetone or methyl alcohol have been taken up due to this condition of unsaturation. Such a coupling would probably result in a permanent adsorption of the polar sorbate molecules and may be objected to on that account. Nevertheless we were never able to remove a considerable amount of the sorbed vapors from the resin samples in a closed desorption system in which the vapor pressure was never greater than 2 mm of mercury for a ten day period. Experiments were made with a cellulose acetate sample and a considerable hysteresis was observed. However, there was never any difficulty in removing the methyl alcohol and acetone vapors at very low pressures.

It is also of interest to note that the resins took up the initial vapors of methyl alcohol more rapidly than those of acetone, although the materials are actually more soluble in the latter substance. This suggests that the smaller molecule was better able to penetrate the structure of the resin. However, our data must be considered insufficient to establish this as a general conclusion, since only two kinds of vapor were considered.

Molecular or Particle Weight. The experimental work of this article has made it possible to make several statements with regard to the structure of the glyptal type of resin. Of necessity these statements have been largely qualitative in nature. Perhaps the most important question to be answered is whether the fundamental structural units are giant molecules (sometimes called macromolecules) or micells. We have expressed our opinion in favor of the macromolecular structure because of the changes in the position and shape of the sorption isotherms for the several resins. The further conclusion has been drawn that the size of these giant molecules, particularly as regards their length and complexity, is increased as the time of the curing process is extended.

However, this research may be considered to be only the beginning of a number of studies which may be expected to lead to the construction of a model which will represent the physical and chemical behavior of the resin. The most immediate and important single task seems to be the determination of the molecular weight, because the properties of the material will certainly depend upon it. There are several methods available to us which should make this possible, the most promising of which are viscosity and dielectric constant studies of the resins in dilute solution. The theory by which the viscosities of the dilute solutions may be related to the molecular weights has recently been reviewed by Staudinger,⁶ so that it will not be given here. The method which involves dielectric constant determinations is an application of the dipole theory of Debye. It depends upon the fact that owing to the frictional resistance of the medium to the rotation of suspended molecules or particles a finite time is required for their orientation in an alternating electrical field. If the frequency dependence of the dielectric constant is determined for such a system of electrically dissymmetrical particles dissolved in a liquid medium there will be found to be a region in which the dielectric constant decreases as its

⁶ Z. physik. Chem., 153, 391 (1931).

frequency is increased. The theory, which has been discussed by Marinesco⁷ and also later by Williams and Oncley,⁸ expressed the size and therefore the weight of the dissolved macromolecule in terms of the observed critical frequency and the true inner friction constant of the medium. Both types of molecular weight study are now in progress in this laboratory.

Summary

1. An apparatus for the study of the sorption of vapors in a gas free atmosphere has been described. It makes use of a quartz balance of the McBain-Bakr type.
2. The sorption and desorption of acetone and methyl alcohol vapors by glyptal resins maintained at 35° and 50° have been systematically investigated.
3. It has been possible to draw a number of conclusions and make several calculations from these data, as follows:
 - a. Equilibrium isotherms characterize the resin as a typical swelling gel.
 - b. The model chosen to represent the glyptal resin, based upon the assumption of giant molecules as the fundamental structural units, is believed to be consistent with the experimental results.
 - c. The first part of the sorption curve is probably due to a surface adsorption, while the last part is due to the purely physical process of the condensation of the vapors in capillary spaces. The transition from one process to the other is indicated by an intermediate region.
 - d. For the cured glyptal resins there are indicated a more firmly knit structure and a larger molecular or particle size. These changes become more and more pronounced as the time of an arbitrary curing process is increased.
 - e. The free energy change as the sorption process at 35° and 50° continues has been calculated.
 - f. From the free energy changes and their temperature coefficients the differential heats of the sorption process have been calculated. These data indicate that the last sorption process is one of simple condensation of the vapors in the capillary spaces.
 - g. Calculations have been made for the size of the interconnecting capillaries in the partially swollen gel. These capillaries have been formed by the filming of the structural units in the first stages of the sorption process.
 - h. The tendency for a resin to become completely dispersed in a solvent is shown to decrease as the time of the curing process is increased.
 - i. The ability of the resins to retain considerable amounts of adsorbed vapor is commented upon.
 - j. It seems probable that except for the very low pressure regions any hysteresis observed is apparent rather than real. This is indicated not only by the experimental data but also by thermodynamical considerations.
4. Corresponding data were obtained for a sample of cellulose acetate and its behavior was compared with that of the several glyptal resins.

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⁷ J. Chim. phys., **28**, 51 (1931); Kolloid-Z., **58**, 285 (1932).

⁸ J. Rheology, **3**, 271 (1931).

FILTRATION PHENOMENA IN COLLOIDS

BY MAY ANNETTS

Colloidal solutions are usually assumed to be unaffected by filtering. But in some cases it has been found that filtering produces important changes—it is the purpose of this paper to outline and explain these changes.

In the course of some recent experiments the following curious effects were observed with Arsenious Sulphide Sol.

(1) The conductivity decreases, sometimes as much as 50%, when it is passed through a filter paper. One would expect that, if the conductivity changed at all, it would increase, due to the addition of electrolytic impurities from the filter paper.

(2) When the colloid is repeatedly passed through the same piece of filter paper its conductivity decreases to a constant value—Graph I.

(3) Repeated filterings of the colloid, each time through a fresh piece of filter paper, cause the conductivity to decrease to a minimum and then increase. These results are shown in Graph II.

(4) The conductivity of a sol which has been filtered, one or many times, increases when it is allowed to stand for some time after filtering—Table I.

1

TABLE I

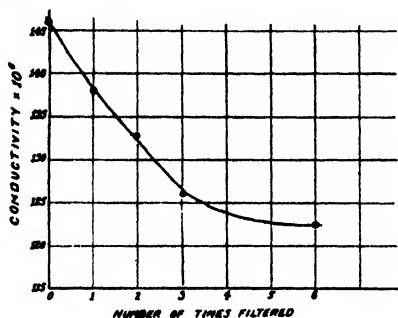
No. of times filtered	Conductivity $\times 10^6$	
	11 A.M.	4 P.M.
0	167	167
1	77.5	92.0
2	49.5	58.0
3	47.7	55.8
4	55.5	57.7

(5) Sols which have been filtered many times coagulate on standing; in fact, if filtering is continued long enough, the sols will filter only very slowly and finally coagulate as they filter.

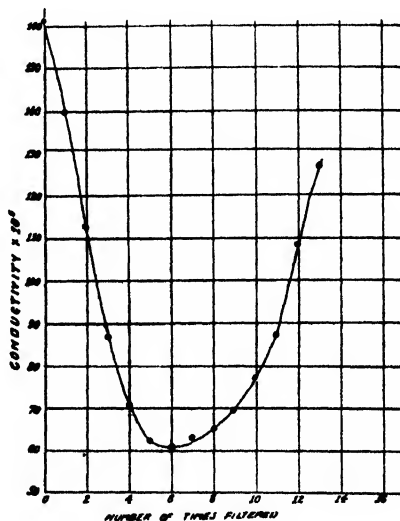
(6) That the effect is dependent on the amount of sol filtered is shown in Graphs III and IV. In Graph III various amounts of sol are filtered, each through a separate piece of filter paper; in Graph IV 25 cc samples are successively filtered through the same piece of paper, the filtrates being kept separate.

(7) The effects are larger when low grade filter paper is used than when especially prepared ashless paper is used, further the effects are reduced by successive washings of poor filter paper with distilled water. The results listed above were obtained using Whatman's No. 1 paper washed with distilled water.

In an attempt to isolate the material causing the initial decrease in conductivity, series of readings were taken using various components of the sol. Each series consisted of conductivity measurements after successive filterings, using a fresh piece of filter paper for each filtering. The results for distilled water, Arsenious Oxide, and Hydrogen Sulphide are shown, from right to left, in Graph V. None of these curves shows the initial decrease which characterizes Graph II. It was therefore thought that the effects might be in some way connected with the colloidal state, so measurements were taken of the conductivity before and after once filtering various sols. Results are shown in Table II. It will be noticed that a decrease occurred only in the two cases where we have both free hydrogen ions and rather high conductivity. Since



GRAPH I



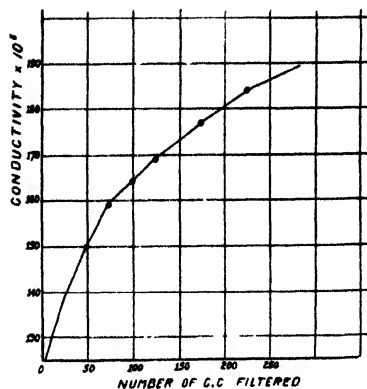
GRAPH II

TABLE II

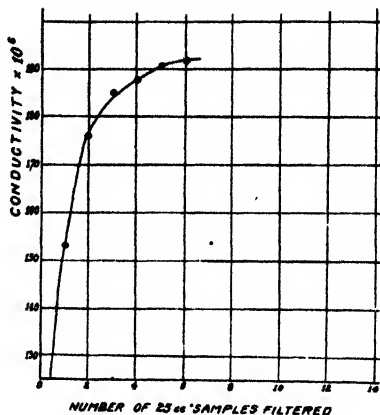
Name of sol	Conductivity $\times 10^6$	
	Before Filtering	After Filtering
Copper	24.6	60.2
Gold (Zsig.)	1400	1400
Gum Mastic	18.3	41.5
Prussian Blue	58.2	88.2
Ferric Hydroxide	3540	3330
Green Gold (Catechol)	864	725

filter paper has a negative charge it might be expected to adsorb hydrogen ions—which would decrease the conductivity. Measurements of pH were therefore made using a quinhydrone electrode with a calomel half cell and potentiometer. The pH was found to increase linearly with the number of times filtered, whatever the material used, and irrespective of whether the conductivity was increasing or decreasing—see Graph VI.

This suggests that the observed results on filtering may be explained as due to the combination of two effects, (a) an increase in conductivity of the sol due to the addition of electrolytic impurities dissolved from the filter paper,



GRAPH III

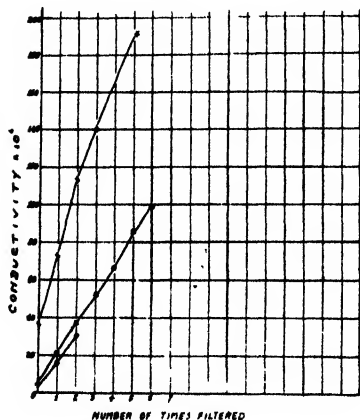


GRAPH IV

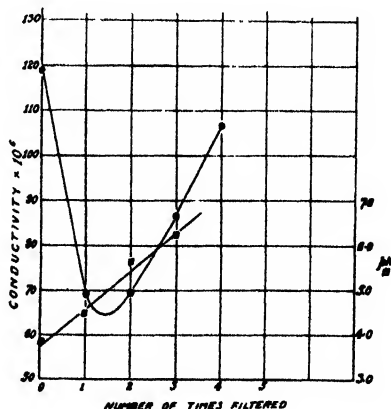
(b) a decrease in conductivity of the sol due to the adsorption of hydrogen ions by the filter paper. Effect (a) will be large when the initial conductivity is small, i.e., when the total number of ions already present is small. Thus when the number of free hydrogen ions is large and the conductivity is large, effect (b) will be large and effect (a) small, so that the resultant effect will be a decrease in conductivity; whereas, when the number of free hydrogen ions is small and the conductivity small effect (b) will be small and effect (a) large, so that the resultant effect will be an increase in conductivity.

If the above reasoning is correct, a dilute solution of hydrochloric acid might be expected to show a decrease in conductivity on filtering, and a sodium chloride solution of the same strength an increase in conductivity. Experiment verifies these predictions. The curve for conductivity of hydrochloric acid with successive filterings is shown in Graph VI.

If the amount of electrolytic material in the filter paper is small, these hypotheses explain why the effect is dependent on the amount of sol filtered,



GRAPH V



GRAPH VI

and why a constant value of the conductivity is obtained by filtering repeatedly through the same piece of paper. Further, it is consistent with the above that the effects are larger with low grade paper than with especially prepared ashless paper; though to explain the larger decrease in conductivity with the poorer paper we must assume that the impurities are responsible for part of the adsorption of ions.

The behaviour of hydrogen sulphide solution may also be accounted for on this theory. It is very weakly dissociated and hence has few free hydrogen ions, while its conductivity was quite low (about $1/5$ that of arsenious sulphide sol) for it was prepared from distilled water.

An arsenious sulphide sol is stabilized by hydrogen sulphide adsorbed around the particles. Thus when few hydrogen ions are removed from the intermicellar fluid equilibrium is destroyed and part of the hydrogen sulphide from the double layer released as free ions. This explains the increase in conductivity and pH on standing, also the decrease in stability of the colloid with successive filterings.

Let us consider a sample of arsenious sulphide sol. Before filtering its pH was 4.05 and its resistance 3800 ohms at 25°C , in a cell whose constant is 0.33. After filtering once its pH became 5.35 and its resistance 6900 ohms at 25°C .

Before filtering, no. of hydrogen ions per cc = $6.2 \times 10^{23} \times 10^{-3} \times .89 \times 10^{-4} = 5.5 \times 10^{16}$. After filtering no. of H^+ ions per cc = $6.2 \times 10^{23} \times 10^{-3} \times .45 \times 10^{-5} = 2.8 \times 10^{15}$. No. of H^+ ions lost = 5.2×10^{16} . The effective current produced by these is $(5.2 \times 10^{16}) (1.59 \times 10^{-19}) (.00349) = 2.9 \times 10^{-5}$ amps. The original conductivity of the sol = $.33/3800 = 8.7 \times 10^{-5}$ reciprocal ohms per cm^2 . After filtering once conductivity of the sol is $.33/6900 = 4.8 \times 10^{-5} \text{ cm}^2$. Therefore loss in conductivity is 3.9×10^{-5} . Loss caused by the removal of hydrogen ions is 2.9×10^{-5} . So that the filter paper must adsorb some ions other than the hydrogen, as one would expect.

The linear relation between pH and number of times filtered means that the number of hydrogen ions adsorbed, y , is proportional to the number of hydrogen ions present, C i.e. $y = aC$ where a is a constant. The average of several sets of readings gives $a = 0.9$ which means that practically all the free hydrogen ions are adsorbed in the first few filterings.

From the resistance changes after many filterings we can calculate the equation representing the addition of electrolyte from the filter paper to the sol. It is found that the change of resistance on filtering, y , is proportional to the square of the resistance before filtering, R i.e., $y = bR^2$. Since this equation holds for all but the first few filterings, the adsorption of ions other than hydrogen must take place during the same time as the addition of hydrogen ions.

Thus changes in conductivity, pH, and stability may be expected to accompany the filtering of suspensoid sols.

In conclusion, the author wishes to express her sincere appreciation to Prof. E. F. Burton of the Department of Physics at the University of Toronto, for his helpful suggestions and advice throughout the investigation.

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REVIEW OF RESEARCH ON CANE WAX IN RAW AND REFINED SUGARS

BY C. F. BARDORF AND J. A. B. BALL

Introduction

The object of this paper is to bring under review a few of the practical aspects of colloidal phenomena in the sugar industry and more specifically those due to Cane Wax.

The complex nature of the juices from the sugar cane and the sugar beet soon obtruded itself upon the attention of the pioneers of the industry, and there is no doubt that the now universally practiced diffusion of beet chips (cossettes) was largely influenced by Graham's classic studies. In the case of beet root tissues the application was obvious. Each tiny cell in the root can be regarded as a dialysing sack, and as such can hold back a large proportion of the colloids and allow the crystalloids to pass into the diffusion water.

In connection with cane juice, however, diffusion processes appear to offer insuperable difficulties. Grinding and milling of the cane is therefore the almost exclusive practice by which a high yield of sugar can be obtained from the cane.

But by this method a large percentage of the colloidal substances are forced into the juice and can be only partially removed by processes more or less based on a common principle.

Non-Sucrose Substances in Cane Juice

As the major part of the work on sugar juice colloids has been directed to those in sugar cane juice, it may be well to give these exclusive attention. But it may be mentioned, in passing, that some thirty years ago the senior author incidentally isolated a quantity of beet sugar wax, which, unfortunately, received only casual attention at the time. This wax, though chemically different from cane wax, had similar physical properties. It contained much nitrogen; on dry distillation it yielded an oil of pyridine-like odor and from an alcohol extraction a wax was obtained quite similar to the alcohol soluble portion from cane wax.

The juice expressed from the cane by the ponderous rollers of modern cane mills is a muddy, olive green or brownish liquid, laden with solid particles ranging in size from macroscopic masses to the ultramicroscopically divided emulsoids—the cane wax complex which has of recent years employed the attention of industrialists and chemists.

In the "mixed" juice, *i.e.*, the united juices from all the sugar mills in tandem, many substances may be found which contribute to the colloidal phenomena in sugar solutions. Some of these substances can be removed easily, while others pass through, in an exceedingly small amount, into the best products of the refiner's art.

Listing the suspensoid particles roughly in the decreasing order of their size, we have bagacillia (small pieces of cane tissue) fine sand, clay, insoluble organic salts of calcium, and then the true dispersoids, such as colloidal silica, and other non-dialysable substances; proteids and pentosans, pectin, etc., and lastly gums and waxes which assume suspensoid and emulsoid forms when the juices are heated or when the defecated juice is concentrated. Concentrated, defecated juice, generally known as "syrup" is the "meladura" of Latin America.

Because of the persistent migration of the cane wax complex through all the processes of sugar making,¹ it may be inferred that it is present in a very minute state of dispersion. Cane wax is undoubtedly the most troublesome of all impurities which has to be dealt with by the defecation methods applicable on an industrial scale, because it adheres so tenaciously to all solids it may contact.

Colloids in Mixed Cane Sugar Juice

Confining ourselves for the moment to the consideration of mixed cane sugar juice we have an impure, thin (15% solids) sugar solution copiously laden with suspended particles. Under defecation methods, common in principle but varied in detail to accord with the nature of the juice, milling practice, etc., the coarser, mechanically introduced particles are, to a large extent, easily separated. Next in order may be considered those substances which are acted upon by heat and chemical reagents. Sulphur dioxide gas being employed for specific purposes only, milk of lime may be said to be the exclusive agent used in practice, and is made to react with the impurities of the juice at a temperature of 100°C or over.

From the so-treated juice, vegetable proteids are coagulated and some organic and inorganic salts precipitated. The flocculent precipitates thus formed trap most of the larger suspensoids and some of the cane wax in the form of emulsoids. These then pass out of the system in the defecation mud. But even with the most carefully controlled pH regulation and the exercise of other precautions, some colloids remain in the defecated juice and require subsequent attention. These highly dispersed substances adhere to and are occluded by the sugar crystals during the process of boiling to grain, be it from raw or refined liquors. When, therefore, raw sugar crystals are dissolved in the refinery the emulsoid colloids in particular, pass through all the stations of the refinery, and some are easily detectable in all granulated sugar. If these raw and refined sugars be specially treated, a variety of unremoved substances can be separated. But one of the difficulties is the question of what procedure shall be followed in the endeavour to separate all suspensoids in order that some reliable quantitative as well as qualitative data may be recorded. Quantitatively it is primarily desirable to determine the total amount of colloids, of all forms, residual in the finished products. The great difficulty in this direction is to free the separated colloids from the last traces of sugar without washing away some of the colloids themselves, which,

¹ Bardorf: Ind. Eng. Chem., 20, 258 (1928).

despite their troublesome nature, are present only in very minute quantities. Qualitative examination has its difficulties because of the complex nature of the colloids, and their tendency to physical change when subjected to ultra-filtration or dialysis. Coagulation takes place so that one colloid traps and occludes another and a pure chemical product is not obtained.

Four Classes of Colloids in Raw and Refined Sugars

From the now large number of investigations on the non-dialysable matter in sugar solutions, syrups and molasses, a fourfold, broad classification has been made by the authors, a classification chiefly based on the physical properties of the complex, *viz.*, (1) Acetone soluble, soft wax; M.P. 52°C; (2) Alcohol soluble brittle wax, M.P. 82°C; (3) Water soluble, not fusible; (4) Insoluble, not fusible, contains nitrogen compounds.

This classification of raw sugar colloids is prompted by the data established by the authors from the dialysis of three typical raw sugars. It was found that the three types, although containing approximately the same percentage of sugar (96%) varied greatly in respect to quality and quantity of non-dialysible matter. Uniform solutions of the three sugars were prepared for dialysis through collodion sacks² and the colloidal matter collected, dried and weighed. The percentage of non-dialysable material so found ranged from 0.15% to 0.38%, but the diversity in its composition was more marked than the relative quantity present. This remarkable diversity was brought sharply to notice upon submitting the complex mass to fractional extraction, using acetone, alcohol and water as the solvents, in the order named.

In the case of the three sugars under examination we obtained the following results:

TABLE I

Non-dialysable Material from Raw Sugars

Source of sugar	% Non-dialysable material
*B. W. I.	0.24
Cuban	0.25
San Domingo I	0.15
†San Domingo II	0.38

* B.W.I.—British West Indies.

† A poor grade of sugar.

The distinctive character of the extracts, as classified in preceding paragraphs, is apparent in this, that if the acetone and alcohol extracts only be taken as denoting the true wax-like material, the B. W. I. sugar contains 0.057%, the San Domingo I, 0.185%, and the Cuban 0.153%, since the fractional extraction of the undialysable portions obtained showed them to consist of the following fractions:

² Cf. Holmes: "Laboratory Manual of Colloid Chemistry," 23 (1928).

TABLE II
Fractional Extracts from Non-dialysable Material

Solvent	San. Dom. I.	B.W.I.	Cuban
Acetone	14.95%	13.14%	27.20%
Alcohol	33.68%	10.80%	34.29%
Water	26.73%	58.50%	{not determined.
Insoluble	24.64%	17.55%	

A further divergence in the composition of the acetone, alcohol and water soluble portions of the colloids is shown in the ash contents of the extracts, as illustrated in Table III.

TABLE III
Ash Content of Wax Complex

Extract	San Domingo % Ash	B.W.I. % Ash
Acetone	0.63	1.55
Alcohol	3.64	19.07
Water	29.87	18.00

Adsorption of Wax Complex (by Comminuted Materials)

After a series of investigations the authors have come to the conclusion that of the many constituents of non-dialysable substances present in raw sugars, there are two, at least, which resist all heretofore practiced technical procedures for their complete elimination from refined sugars, even from those of the highest purity. There are several phenomena which seem to substantiate this opinion, although it is a fact that the acetone and alcohol soluble constituents of the cane wax complex are tenaciously retained by such materials as filter cloth, diatomite, paper pulp and bone black. We have been able to extract appreciable quantities of the wax constituents from the first three mentioned materials. This property of the complex is of significance, since no amount of washing with hot water (90°C) will remove any appreciable amount of it. This is illustrated in Table IV.

TABLE IV
Wax Complex retained by Filter Cloth, Diatomite and Paper Pulp

	Cloth	Diatomite	Paper Pulp
Acetone soluble	0.95%	1.79%	2.74%
Alcohol soluble	0.41%	1.79%	0.94%
Total	1.36%	3.58%	3.68%

A noticeable feature in this table is that although the melting point of the acetone soluble is 52°C, and the alcohol soluble is 82°C, the wax of the lower melting point is more persistently held by the cloth tissue and paper pulp than its alcohol analogue.

In regard to bone black adsorption of the complex, Paine and Badollet³ have investigated the adsorption of what they call reversible and irreversible colloids, and find that bone black exhibits a preferential adsorption for reversible colloids, which, it appears, is dependent on the quality of the bone black—the more active blacks have a decided preference for the reversible form. In this connection the authors would refer to their paper on "Filtrability and Refinability of Raw Sugars"⁴ in which it was pointed out that in their experience with raw sugars from the Uba cane, "the bone char rapidly reached a stage of saturation with respect to colloidal matter, which it then appeared to give up indiscriminately to water or any brilliant syrup . . . heat tends to coagulate the colloids in such syrups."

Paine and Badollet admit that their distinction "reversible" and "irreversible" is more or less arbitrary. They say: "For instance if the period of heating of the dried residue (of colloids) is extended the proportion of water-irreversible colloids is increased, a portion of the reversible colloids becoming irreversible (presumably by hydration)."

In this connection Dr. Steacie, in a lecture at the McGill University, contended that colloidal particles of the same composition assume various physical characteristics dependent upon the numerical conjunction of their molecules. In the light of this statement it would appear that "reversible colloids which may become irreversible" or "emulsoids and suspensoids" merely become terms used to distinguish the varying physical properties of the same colloid.

The numerous "amorphous" activated carbons on the market exhibit properties similar to bone black in the adsorption of colloids, and it is largely to this that they owe their value as auxiliary refining agents.

We can now pass on to an important question, *viz.*: What is the nature of the colloids found in refined sugar products, from the purest white crystals (granulated sugar) to soft sugars of all grades (yellow or brown)?

In so far as no determinations have been made on the distinctive characteristics of acetone and alcohol soluble components of cane wax, we do not know which of the two is the more resistant against complete elimination from the refined sugar product. There are, however, at least two considerations which would lead us to feel convinced that it is the acetone soluble which is present in greater percentages in refined sugars.

In our previous paper⁵ on the subject, we designated the acetone soluble by the letter "G", and the alcohol soluble by "B." These terms were chosen for brevity's sake, G being assigned to the acetone soluble because this fraction was usually of a greenish colour, while the alcohol soluble was brown.

If we now calculate the percentage of the G in the G-B wax extract $100G/(G+B) = \%G$, we obtain certain percentages of G which are quite significant. A study of these percentages would seem to indicate that in those sugar solutions, and the sugars obtained from them, which have received

³ Planter Sugar Mfr., 79, 21 (1927).

⁴ Intern. Sugar J., 29, 375 (1927).

⁵ Bardorf: Ind. Eng. Chem., 21, 366 (1929).

the least treatment or purification, the *G* fraction is present in the neighborhood of 50%, while in similar solutions and sugars therefrom, which have gone through refining processes, the *G* content is over 50%.

Analysis of the data given in Table V, tends to substantiate this contention.

TABLE V
Percent "G" in Raw Sugars and Solutions

Normal raw sugar.....	51%
Crusher juice.....	50%
First Mill juice..	51%
Second Mill juice.....	65%
Defecated juice.....	40 to 60%
Average in Cuban Raw Sugars, three seasons.....	52%
Cuban Raw, 1926.....	49%
Cuban Raw, 1928.....	63%
B. W. I. Raws, 1926....	39%
Final Molasses.....	52%

Percent "G" in materials in contact with sugar solutions during refining

Filter cloth.....	70%
Diatomite.....	50%
Paper pulp washed @ 88°C.....	74%
Paper pulp washed @ 65°C.....	64%
Refined sugars from the vacuum pan.....	72%

A few words of comment may be necessary to explain two or three apparent anomalies in this table. The remarkable rise of *G* wax in the second mill juice is due to the addition of water, known as (maceration or inhibition water) to the bagasse, thus augmenting the emulsifying action of the rollers. The *G* percentage is nearly always highest in juice from the second roller set, as it is here that the most of the colloids are forced into the juice. From actual determinations of *G* in juices flowing from a four tandem mill the percentages were respectively 47, 67, 55 and 65. The crusher juice was 46%.

The high percentage of *G* in Cuban raw sugars of 1928 is consequent upon the large proportion of old and burned cane ground at the mill from which the sugar was sampled. That only 50% of *G* was found in the diatomite lies in the fact that the filter aid was used exclusively, in this case, for the pressing of liquor from washed raw sugar crystals, and must therefore contain the same relative percentage of *G* as the raw sugar itself.

Minute Presence of Colloids in Granulated Sugar

There are several further facts to substantiate the conclusions drawn from the acetone soluble percentage of wax extracts in raw sugar products as compared with the percentage in refined products.

A standard grade of granulated sugar may certainly be regarded as one of the purest of food products, being comparatively chemically pure. For in-

stance, ten samples of such sugars were found to contain ash ranging from a minimum of 0.002% to a maximum of 0.016%, having an average of only 0.008%.

While the presence of colloidal matter may almost always be observed, the quantity present must be exceedingly small. The authors know of no direct reliable method for the quantitative determination of colloids in granulated sugar, but there are several by which it may be inferred that the colloidal content is 10 per million parts of sugar, or even less. To determine this emulsions were made quantitatively of extracted fractions of acetone, alcohol and water soluble colloids, and their opacities and colouring qualities studied.

Acetone Soluble Wax the Predominant Colloid in Granulated Sugar

To three separate volumes of a 50% solution of water-white granulated sugar were added the three fractions of colloids respectively, in the proportion of 10 parts in 1,000,000, brought up to 100°C and well shaken. Examination by the Lovibond tintometer showed that the acetone soluble fraction imparted one unit of colour, the alcohol soluble sixteen units, and the water soluble eighty units. But the tint imparted to the solution by this quantity of the water soluble fraction was far greater than would ever be met with in any granulated sugar of reasonably good quality. On the other hand the acetone soluble wax produces a more pronounced "colloidal haze" than does the alcohol soluble, and the water soluble the least of all. This phenomenon is more definitely displayed by comparing the relative strengths of Tyndall cone produced in the solutions under examination.

Closely related to this question, Badollet is developing a particularly interesting apparatus for the ultra-microscopic photography of colloids. He has applied this apparatus, in its present stage of development, to the examination of granulated sugar solutions, and has produced a large number of photographs in the study of this problem. Here again we have a confirmation of the occlusion of colloids by the growing crystals, even when the sugar liquors are of high purity and brilliant appearance when viewed by transmitted light.

We have a remarkable illustration of how the colloids are more or less occluded in proportion to the quantity present in the liquor charge from which the crystals are grown. A liquor of lower sugar purity, but relatively free of colloids will give a sugar exhibiting a feebler Tyndall cone than one boiled from a liquor of higher purity but more charged with colloidal particles. (Exhibit photographs):

"B" from high liquors.

"S" from colloid free syrup.

"O" from white liquor, but containing colloids.

Remelt.

Lastly, if a granulated sugar of large grain be washed with cold water so that in three consecutive washings each will contain about one-third of the sugar, the solution representing the outer layer of the crystal will invariably

show the strongest Tyndall cone, while the third washing, representing the core of the crystal, will show the dimmest cone. From these and other considerations the authors conclude that of the four classes of non-dialysable material in raw sugars, the insoluble fraction is completely removed in the preliminary steps of the refining operations, *i.e.*, defecation and filter pressing. Of the other three the water soluble is absorbed up to 90 or 95% by bone black, but the acetone and alcohol soluble colloids migrate through all the stations of the refinery, and their presence is detectable in all granulated and soft sugars.

From these data we may hope that by the refined optical methods, now being developed, some definite quantitative and qualitative information will eventually be obtained. Closely related to Badollet's photographic work is that of Balch⁶ with the Spectrophotometer and Zerban and Sattler⁷ with the recently introduced Pulphrich photometer. Zerban and Balch have evolved mathematical formulae from which both investigators have been enabled to construct instructive tables on Tyndall cone intensities. Zerban has shown that in this respect certain anomalies have still to be investigated before the light phenomena can be thoroughly understood.

For a fairly complete bibliography of the large number of articles on Cane Juice Colloids, Farnell's⁸ report may be consulted. In this report the chemical as well as the physical properties of the colloids are discussed in many important details; thirty-three references are given.

Much of the work above alluded to had to be carried out on sugar Centrals themselves, and the authors wish in particular to thank the Eastern Cuban Sugar Corporation, and the American Sugar Refining Company for the co-operation and hospitality of their Cuban estates, and Dr. Schlegel of the National Sugar Refineries, for his help in collecting, washing, and sending samples of paper pulp used for the filtration of raw sugars.

*St. Lawrence Sugar Refineries,
Montreal, Canada.*

⁶ Ind. Eng. Chem., Anal. Ed., 3, 124 (1931).

⁷ Ind. Eng. Chem., Anal. Ed., 3, 326 (1931).

⁸ Intern. Sugar J., 26, 420 (1924).

ON THE NATURE OF COAGULATION VISCOSITY, AND THIXOTROPY IN COLLOIDAL SYSTEMS

BY S. S. KISTLER

Introduction

The most prominent division of colloids into classes is that into lyophilic and lyophobic. Many phenomena have been more or less satisfactorily explained on the basis of the differences in the relationship of the colloidal particle to the dispersion medium in these two groups. It has been assumed with considerable justification that the lyophilic particle is closely associated with a comparatively large quantity of the dispersion medium, and numerous investigations have had as their goal the measurement of the amount of "bound" solvent. Although the results unquestionably lead to the conclusion that there are large differences in this relationship of dispersed to dispersing medium, quantitatively there has been little agreement between the various methods used.

The conception of "bound" solvent has led to the general conclusion that a certain amount of the solvent is held in more or less of a rigid condition within or surrounding the micelle. The author¹ has shown quite conclusively, however, that at least in the case of certain of the hydrated sols and gels, the amount of water that can be held in anything like a rigid condition must be very small. The fluidity of the water in these cases investigated was found to be not widely different from that of pure water. Also, Briggs² in a recent very illuminating article has clearly pointed out that "bound" water in its usually accepted meaning is purely a fiction.

In spite of these objections, nevertheless, qualitatively there is no question of the large differences between the lyophilic and lyophobic colloids and the concept of solvation will undoubtedly continue to be useful although its exact meaning remains unknown.

The Existence of Cybotactic Complexes in Liquids. In recent years considerable progress has been made in our understanding of the structure of liquids, and I feel that the time has come when these findings can be applied to our knowledge of colloidal systems with much clarification of mooted subjects. X-ray investigations³ apparently indicate conclusively that within liquids the molecules are constantly associating into evanescent complexes of crystal-like arrangement. Even in the case of liquid mercury Debye⁴ has demonstrated the existence of these complexes. That these complexes must

¹ Kistler: J. Phys. Chem., 35, 815 (1931).

² J. Phys. Chem., 36, 367 (1932).

³ Stewart and Morrow: Phys. Rev., 30, 232 (1927); Stewart: Rev. Modern Phys., 2, 116-22 (1930).

⁴ Debye and Menke: Physik. Z., 31, 797 (1930).

be widely different from true crystal nuclei seems certain from the fact that, although Stewart estimates that at any one instant a large fraction of the molecules in a liquid are thus associated, numerous liquids may be undercooled for long periods of time without crystallization. Richards and Harris⁵ conclude from their observations on the scattering of light that in undercooled liquids there are evanescent amorphous complexes. Whether these amorphous complexes of Richards and Harris are the same as the crystal-like complexes of Stewart, Debye, and others, it is impossible to decide. It may be that they are the same but only upon undercooling of the liquid do the densities of the liquid and complex differ enough to scatter light appreciably. Stewart has applied the term cybotactic complexes to those that show evidence of crystal-like structure with X-rays. His definition is sufficiently broad and vague, however, so that for lack of a better term, I shall refer to all associations of molecules into transitory groups as cybotactic complexes and for convenience shall refer to them as cybomas.

Whatever the nature of the cybomas, their existence can scarcely be questioned. Within a liquid the molecules must be constantly associating into cybomas, remaining thus associated for a brief moment and dissociating again only to reassociate with other neighbors. How rigid these associations may be remains at present unknown, but it seems very reasonable to assume that for the brief period of its existence, a cyboma will behave as a single particle and go through Brownian movements. In fact, it seems a perfectly reasonable assumption that any one complex may not disappear in entirety but rather that it is experiencing growth and decay at the same instant. In other words, the probability for the existence of any small group of molecules within the larger complex in a rigid framework is independent of the probability for the complex as a whole, so that while new molecules are adding to the surface of the complex, older portions are at the same time liquefying. A single cyboma, therefore, may progress through the liquid by growth on one side and decay on the other. It may branch and the branches quickly split off or it may liquefy as a whole.

If there is some sort of orientation of the molecules within the complex, growth by orientation of liquid molecules at the surface may be more probable than the sudden association of a group of neighboring molecules into a coherent mass. Regardless of how these cybomas arise, it is to be expected that they will on the average consist of relatively few molecules and, therefore, will diffuse rapidly compared to the velocity of a moderate sized colloidal micelle.

Influence of the Surface of a Colloidal Particle on Cyboma Formation

If we consider an imaginary boundary in the undisturbed liquid, an equal number of cybomas will cross from each side in unit time due to Brownian motion. Suppose, however, that this boundary is replaced by the surface of a colloidal particle; there will now come to the surface in unit time the same number of cybomas as would have crossed the imaginary boundary. But the

⁵ J. Am. Chem. Soc., **54**, 3799 (1932).

surface may materially influence the number that progress outward from it. In other words, the substitution of a solid surface for the imaginary boundary may materially affect the equilibrium conditions at this boundary.

Three possibilities exist: (1) The cybomas coming to the surface are reflected from it so that the same number will be leaving as approaching, or in other words, the equilibrium will be undisturbed. (2) The cybomas in contact with the surface disappear more rapidly on the average than those in the center of the liquid. Under these circumstances there will be fewer cybomas leaving the surface than approaching it, and when an equilibrium is established the concentration of the cybomas in the neighborhood of the colloidal

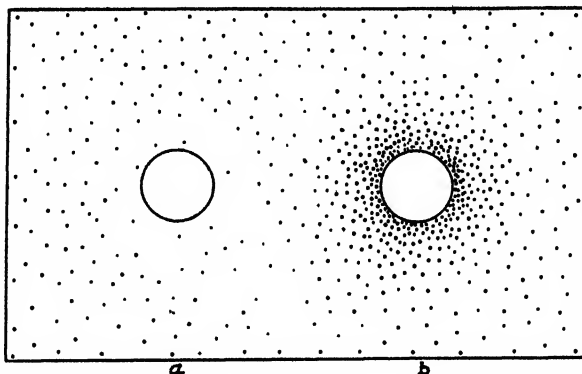


FIG. 1

Schematic arrangement of cybotactic complexes around a lyphobe and a lyophile particle

particle will be less than in the center of the liquid. (3) At the surface of the particles, the probability that neighboring liquid molecules will associate into a more or less rigid framework will be greater than the average for the liquid. In other words, more cybomas will leave the surface than will approach it, and when the steady state is reached there will be a concentration gradient established diminishing with distance from the particle. The second and third possibilities are represented by a and b respectively of Fig. 1. It seems probable that deviations from case (1) will be greater with (3) than with (2) since the concentration gradient built up in (2) depends on the number of cybomas in contact with the particle surface, whereas in case (3) it is independent of the number of cybomas present and depends only on the interrelationship between the surface and the liquid molecules.

The number of cybomas in contact with unit area of a surface at any one instant must be small compared to the number of liquid molecules in contact at the same instant.

If we assume that there are a cybomas per second formed per unit volume and that there are kn_0 cybomas vanishing, where n_0 is the number present per unit volume, in the steady state

$$a = kn_0 \quad \text{or} \quad n_0 = a/k$$

Assuming case (3), that is, a concentration of cybomas at the surface greater than n_0 , and considering the surface to be plane it can be shown⁶ that

$$n' = P'e^{-\sqrt{k/D}x}$$

where D is the diffusion coefficient, n' is the difference between the concentration at the distance x from the surface and n_0 , and $P' = n'$ when $x = 0$. The expression for variation in concentration with distance from the surface of a sphere is⁷

$$n' = \frac{r_0}{r} P' e^{-\sqrt{k/D}(r-r_0)}$$

where r_0 is the radius of the sphere.

Since we are totally in the dark as to the average size and average life of these cybomas, the best we can do is to make some reasonable assumptions and see where they lead us. Assuming that the average cyboma in water contains 10 molecules, that its density is the same as water and that its average life is 10^{-6} seconds, the curves of Fig. 2 were obtained for variation in n' with distance from a flat surface, a spherical particle 400 Å in diameter, and a spherical particle 100 Å in diameter.⁸ The concentration at the surface,

⁶ In the stationary state, the number of complexes crossing one cm^2 of a plane parallel with the surface at a distance x will be $-D \, dn/dx$ per second, and this must be equal to the number of complexes in excess of n_0 vanishing per second in a column of one cm^2 cross-section extending from the plane outward to infinity. In symbolic form,

$$-D \frac{dn'}{dx} = \int_x^\infty kn' dx$$

differentiating

$$D \frac{d^2n'}{dx^2} = kn'$$

which gives on integration,

$$x = C_2' - \sqrt{D/k} \ln(n' + \sqrt{n'^2 + C_1/k})$$

Now when $x = \infty$, $n' = 0$ and therefore $C_1 = 0$. Postulating that when $x = 0$, $n' = P'$ we get

$$n' = P' e^{-\sqrt{kx/D}}$$

⁷ Starting with the same assumptions as in note 6, the number of complexes radiating from a particle and crossing concentric spherical envelope of radius r is

$$4\pi r^2 D \frac{dn'}{dr},$$

therefore

$$-4\pi r^2 D \frac{dn'}{dr} = \int_r^\infty kn' dv = 4\pi k \int_r^\infty n' r^2 dr.$$

Differentiating

$$\frac{d^2n'}{dr^2} + \frac{2}{r} \frac{dn'}{dr} - \frac{k}{D} n' = 0.$$

The general solution is

$$n' = \frac{C_1}{r} e^{\sqrt{k/D}r} + \frac{C_2}{r} e^{-\sqrt{k/D}r}.$$

Now introducing the conditions that $n' = 0$ when $r = \infty$ and that $n' = P'$ when $r = r_0$,

$$n' = \frac{r_0}{r} P' e^{-\sqrt{k/D}(r-r_0)}.$$

⁸ The radius of a cyboma containing 10 water molecules will be about 4.2×10^{-8} cm. Now from Stokes' law and kinetic theory.

$$D = \frac{RT}{6\pi\eta rN} = 5.2 \times 10^{-8},$$

where η is the viscosity of water (0.01), r the radius of the cyboma and N the number of molecules in one gram mole. From the assumption that the average life is 10^{-6} , $k = 10^6$, and $\sqrt{k/D} = 4.4 \times 10^5 \text{ cm}^{-1} = 4.4 \times 10^{-3} \text{ Å}^{-1}$.

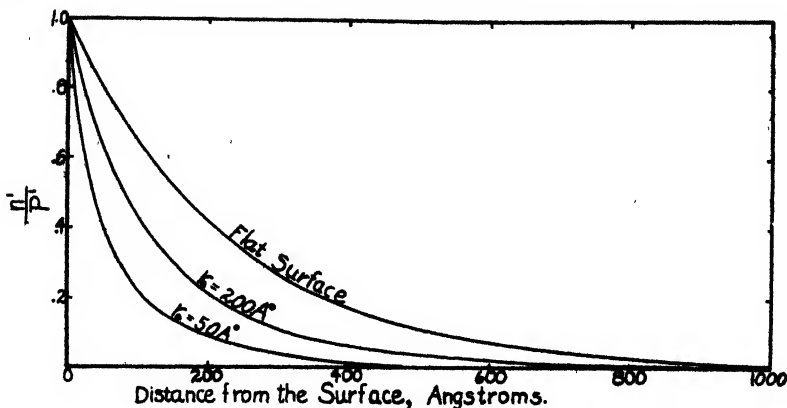


FIG. 2

Variation in concentration of cybomas with distance from flat and spherical lyophilic surfaces

P' , is taken as unity. This value will undoubtedly be widely different for different surfaces. What its magnitude is can only be guessed, but it can easily be such that the diffusion pressure is that of a half molal solution. The influence of a surface at relatively large distances out into the liquid is strikingly shown by this figure.

Coagulation

A colloidal solution in which the micellar surfaces either decrease or do not affect the number of cybomas in their immediate neighborhood will be essentially unstable and will flocculate rapidly unless it can depend upon electric charge or some other means of keeping the particles from coming together and adhering. This is the case with the lyophobic colloids. If the concentration of the cybomas decreases with decreasing distance from the surface there will actually be a difference in the diffusion pressures due to the cybomas on the adjacent and far sides of two micelles near together, which will manifest itself as though there were an attractive force drawing the particles together. Fig. 3 represents this situation. That means that in such a sol the particles must have high electric charges in order to remain permanently dispersed. The addition of a small amount of precipitating ion, while not sufficient to neutralize the charge, may reduce it to the point where a particle of higher than average energy can penetrate through the electric atmosphere of another particle and adhere. This situation is strikingly parallel with that found in the typical lyophobic sols. The sols become unstable at Zeta potentials rather widely removed from zero. Also Smoluchowski⁹ in the derivation of his familiar equation for rate of flocculation found it necessary to postulate the existence of an attractive force extending beyond the surface of a colloidal particle, although there has never been a satisfactory explanation of the nature of this force.

⁹ *Physik. Z.*, 17, 557, 583 (1916); *Z. physik. Chem.*, 92, 129 (1917).

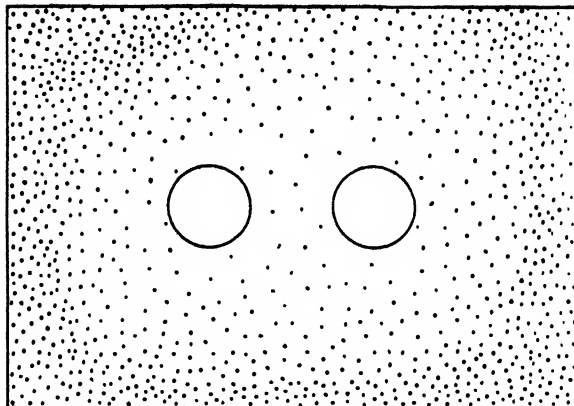


FIG. 3

Conditions surrounding two adjacent lyophobic particles, showing how they are forced together in the absence of electric charges.

Not only may an adsorbed substance affect the Zeta potential but it is highly probable that it also affects the relationship of the surface to the cyboma concentration. Thus it is possible that a sol that fits case (1) or even case (3) above may be so changed by the addition of an electrolyte or other substance that this attractive force will be brought into play and the sol will behave as a typical lyophobic sol. Such cases are rather common. For example, although aluminum oxide and vanadium pentoxide sols are classed among the hydrophilic sols, they are readily sensitized by various means so that very small quantities of electrolytes will precipitate them. The opposite may also be true and an added substance can very much increase the stability of a sol such as, for example, the addition of a protective colloid or the protective action of polyhydric alcohols on certain sols.

In the case where the concentration of cybomas in the immediate neighborhood of a micelle is considerably larger than that in the mass of the dispersing

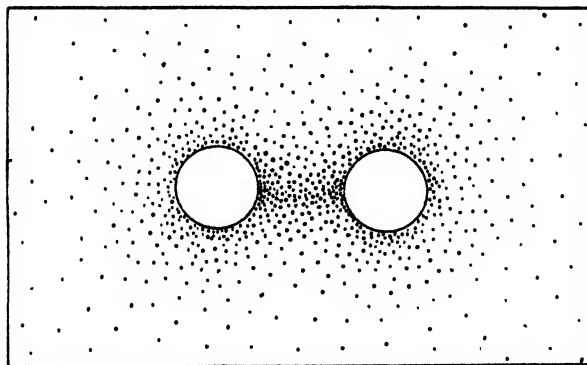


FIG. 4

Conditions surrounding two adjacent lyophilic particles, showing how cyboma pressure is built up between them.

phase, when two particles approach each other the conditions set up will be similar to that depicted in Fig. 4. There will be a decided increase in concentration of the cybomas in the region between the micelles which will have the effect of increasing the cyboma pressure on the particles and forcing them apart. The exact mathematical treatment of the rise in pressure on a micelle as it approaches another is very difficult, but it can be approximated by assuming that this rise in pressure will be proportional to the rise that would be produced if the micelle were surrounded by an envelope, of radius equal to half the distance between micelles, that is impervious to cybomas. In other

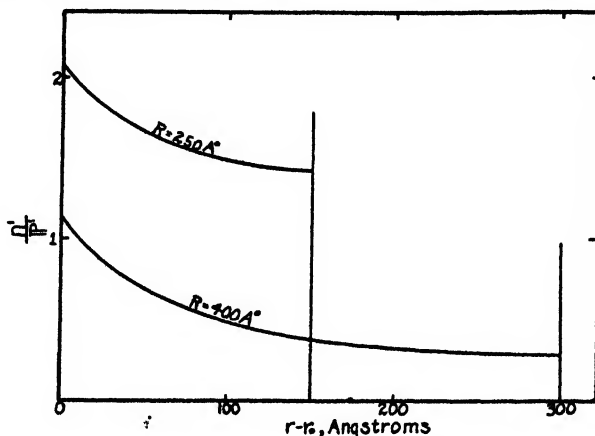


FIG. 5

The variation of n' with distance from the surface of a spherical particle of radius 100 \AA when the cybomas are prevented from diffusing beyond an envelope of radius R .

words, all the cybomas produced by the surface would have to remain within this spherical envelope. Fig. 5 represents the effect of this envelope radius, R upon n' , the concentration of cybomas. In this figure $2(R-r_0)$ represents the distance separating the micelle surfaces and Π' the pressure at the surface when $R = \infty$, i.e., when there is no interference with the outward diffusion of the complexes.¹⁰

¹⁰ Differentiating the general solution given in note 7, one gets

$$dn'/dr = \kappa/r (c_1 e^{+\kappa r} - c_2 e^{-\kappa r}) - n'/r, \text{ where } \kappa = \sqrt{\kappa/D}.$$

Now where

$$r = R, dn'/dr = 0$$

$$c_1 = \frac{\kappa R + 1}{\kappa R - 1} c_2 e^{-2\kappa R} \text{ and } c_2 = \kappa' P'$$

where

$$\kappa' = \frac{\frac{\kappa R + 1}{\kappa R - 1} c_2 e^{-2\kappa R} + c_2 e^{-\kappa R}}{r_0}$$

Therefore

$$n' = \frac{\kappa' P' \left\{ \frac{\kappa R + 1}{\kappa R - 1} e^{\kappa(r-2R)} + e^{-\kappa r} \right\}}{r}$$

and

$$\frac{P'}{\Pi'} = \frac{\kappa r_0 + 1}{1 - \kappa' \kappa \left\{ \frac{\kappa R + 1}{\kappa R - 1} e^{\kappa(r_0-2R)} - e^{-\kappa r_0} \right\}}.$$

Fig. 6 shows the change of the ratio P'/Π' with changing values of R . Here P'/Π' represents qualitatively the repulsive force acting upon the side of the particle adjacent to another particle as compared to the normal pressure on the side discharging its complexes into free liquid. Here the existence of the equivalent of a repulsive force at large distances is illustrated. In Figs. 5 and 6 it is assumed that the rate of formation of cybomas at a surface is independent of P'/Π' , which seems reasonable within limits.

As one can readily see, this pressure tending to force particles apart will give the sol stability without electric charge and this is the case with the typi-

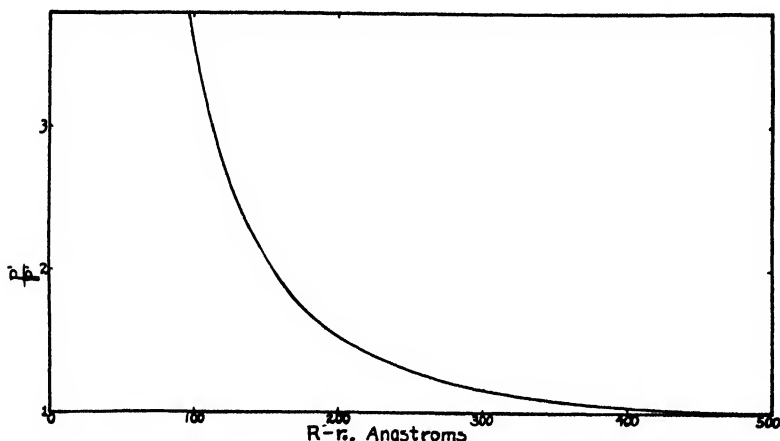


FIG. 6

The variation of the cyboma pressure on the surface of a particle of 100 Å radius produced by variation of the radius of an impermeable envelope.

cal lyophilic colloids such as gelatin or agar. With this type of colloid it can readily be seen from our picture that small concentrations of electrolytes will be relatively ineffectual in causing precipitation.

From what has been said so far, it would be expected that lyophobic colloids would normally require some special means for dispersing them, while lyophilic colloids would tend to disperse themselves spontaneously, a difference which is one of the most characteristic of these two groups.

Again, the same picture that we have drawn would indicate that when rate of diffusion is measured by the diffusion of a sol along a concentration gradient, such as into pure water, the lyophilic particles should diffuse more rapidly than lyophobic of the same diameter due to this repulsion between the micelles with surfaces of type (3). This difference has been observed by Bruins,¹¹ who found that hydrophobic particles diffuse at the expected rate, while hydrophilic diffuse faster. Addition of electrolyte in the latter case decreased the rate, a fact easily explained on the basis of a decrease in the rate of complex formation at the surface. He also noted a parallel decrease in viscosity which is in complete harmony with this view, as will appear later. At first thought it

¹¹ Kolloid-Z., 54, 265; 57, 152 (1931).

might appear that the electric field surrounding the lyophobic particles would produce the same repulsion at a distance as the cyboma cloud, but this is not the case due to the electric double layer, which although diffuse will reduce the repulsion between the particles to a negligible value at a relatively small distance.

The identification of lyophobic and lyophilic sols with types (2) and (3) respectively seems particularly logical since it would be expected that if there is an influence on the formation of cybotactic complexes by a surface, the surface more nearly chemically related to the solvent would be more apt to stimulate growth. In all cases of highly solvated colloids, the solvent and the colloid surface can be shown to be very similar in character. It may be that on solvated surfaces there is a distinct orientation of molecules that induces the orientation and addition of other neighboring liquid molecules upon it. Complexes grow outward from the surface, split off and others appear. Such a particle would appear like a large permanent cyboma seeding the surrounding liquid with its offspring.

Another prediction that comes directly from the interrelationship of the cybomas with a surface concerns the lyotropic series of monovalent cations. It is a common fact that with the more or less hydrophilic colloids such as aluminum oxide the precipitating power of these ions increases in the order $\text{Li}^+ \rightarrow \text{Na}^+ \rightarrow \text{K}^+ \rightarrow \text{NH}_4^+$, while there is practically no difference in their precipitating values with lyophobic sols. One of the most outstanding differences between these ions is the degree of hydration which decreases in the order given. The lithium ion is surrounded by a larger sphere of water molecules and perhaps by a larger number of cybomas than the other ions. The repulsion, therefore, between a lyophilic micelle and a lithium ion will be greater than between the same micelle and any of the other ions and, therefore, when equilibrium is established with a solution of definite concentration the amount of these ions adsorbed will be greater the lower the degree of hydration of the ion. In the case of the lyophobic particle, the establishment of equilibrium will be so much more dependent upon the charges than upon the hydration of the ions that this difference will have a negligible effect.

As two colloidal particles with lyophilic surfaces approach each other, there will be no repulsive force experienced by either as the cyboma clouds interpenetrate until sufficient time has elapsed for the new conditions between the particles to effect a rise in the concentration of the cybomas at the surface of the particle. This time lag means that the faster moving particles will be able to come much closer together before repulsion is experienced and therefore will have much better opportunities to come together and adhere. Since all particles on the average possess the same kinetic energy, the smaller micelles will move faster and have greater opportunities to attach themselves to others. This effect of size will be further accentuated by the fact that the smaller particles have less dense clouds of cybomas surrounding them as is shown by Fig. 2. This means that very small or very large particles in lyophilic sols will not be as common as some intermediate size, or in other words,

the lyophilic sols will tend to have uniform particle size. It is possible that the pronounced uniformity of certain proteins may be thus explained.

The action of a protective colloid is readily understood in the present light. The particles of highly lyophilic colloid surround the lyophobic particle giving it a lyophilic character. Adsorption of the protective colloid can occur even though adhesive forces are negligible, due to the fact that when once the particle with its cyboma cloud has come into contact with the lyophobic particle, there will be a decided difference in diffusion pressure of the cybomas between the particles and on the outside, which will tend to hold them together.

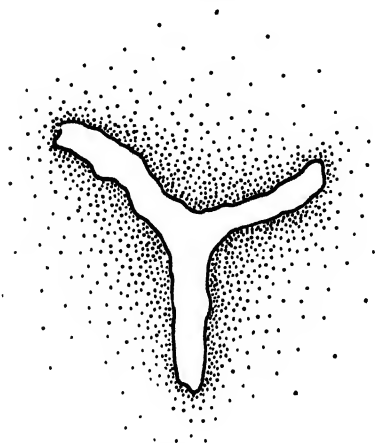


FIG. 7

Distribution of cybomas around an irregular lyophilic body, showing the much decreased density where the radius of curvature is small. Micelles can therefore most readily attach to edges and corners.

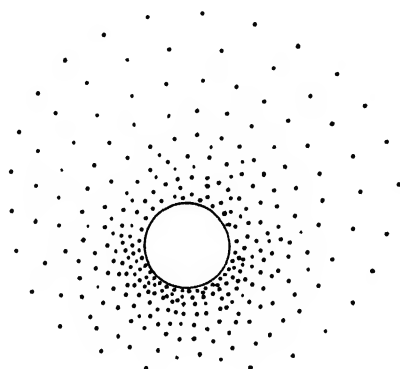


FIG. 8

Conditions surrounding a colloidal particle settling in a gravitational field illustrating the buoyant effect of the cyboma cloud.

The fact that the concentration of cybomas at a given distance from a solvated surface is smaller the smaller the radius of curvature of the surface leads one immediately to the conclusion that under circumstances in which agglomeration may occur, it will be easier for micelles to penetrate the cyboma cloud and attach themselves on edges and corners of a mass already coagulated. One, therefore, would anticipate that the agglomeration of such micelles would lead to the formation of chains, plates, or irregular fibrous or membranous structures rather than solid masses. The conditions surrounding an irregular mass would be somewhat as shown in Fig. 7. This type of structure would tend to surround and occlude large quantities of the dispersing medium and form a semi-solid spongy mass of practically the same volume as the original sol. Such a coagulated colloid we term a gel, and gel formation is one of the most characteristic manifestations of the lyophilic colloids. The strength of such a gel would depend upon forces of cohesion between micelles, as well as upon their shape and the structure of the agglomerated mass.

Probably the stronger the character (3) the stronger will be the gel, due to the more fibrillar structure. Notable exceptions occur to this rule—such as silica

gel, in which the structure is probably not that of agglomerated colloidal particles but is, at least in part, due to what one might term dendritic crystallization.

An interesting possibility is that cyboma clouds surrounding large hydrated molecules such as those of sucrose may have a real influence in preventing crystal nuclei from forming in supersaturated solutions. It is logical that if they are present they will tend to hinder the proper orientation and close approach of sufficient molecules to form a stable crystal nucleus.

It is clear that a cloud of these evanescent molecular complexes surrounding a colloid particle will have a very decided influence upon its rate of sedimentation. As the particle settles through the liquid the complexes diffusing out from the lower side will be continually swept back toward the particle by the counter current of liquid, so that there will build up in the layer immediately in contact with the particle a higher concentration on the lower side and a proportionately lower concentration on the upper than normal. The conditions will be somewhat as represented in Fig. 8. The total effect will be as though a rigid sphere of liquid surrounding the particle were carried along with it. The particle will experience greater resistance than would be predicted by Stokes' Law.

Not only will this effect occur with particles falling in class (3) but it should manifest itself as well in case (2) because in this instance, the approach of cybomas to the lower side of the particle will be aided, while that to the upper side will be hindered and again a differential pressure on the two surfaces will be produced.

Viscosity

One of the most prominent features of colloidal solutions is their viscosity, which has been the subject of numberless investigations, but which as yet has received no adequate treatment. In view of the fact that viscosity of pure liquids itself has not been understood the failure to make marked progress with colloids is not surprising. Recently, however, Andrade¹² and Edwards and Stewart¹³ have indicated the very close connection between the cybotactic complexes and viscosity, which intimates strongly that in this direction also lie large possibilities of application to the colloid field.

Accepting these authors' point of view, which is the most reasonable so far presented, it is evident that the fluid in a colloidal solution of the third type, that is, in which the number of complexes is increased due to the influence of the particle surfaces, will have a greater viscosity. This change of viscosity of the liquid will depend upon the surface character of the suspended particles. Its magnitude cannot at present be predicted, but will probably be small. Since it is a function of the total surface of the colloid, in sols of the same concentration but different particle size, it will be greater the smaller that size, which is one possible explanation of the variations that have been observed.

An influence of larger magnitude than that above will be that of the interaction of the cyboma cloud with the micelle. The same effect as that de-

¹² *Nature*, **125**, 580 (1930).

¹³ *Phys. Rev.*, (2) **38**, 1575 (1931); Stewart: *Nature*, **128**, 727 (1931):

picted in Fig. 8 will come into play but in this case there will be two regions of increased pressure on opposite sides of the particle under shearing stress, as shown in Figs. 9, a and b. Fig 9, a, shows the effect of a low rate of shear in the liquid upon the cloud surrounding the micelle. Here the cloud is distorted and the resultant concentration on opposite sides of the particle will produce equal and opposite forces upon it directed at an angle with the plane of shear, the angle increasing with the rate of shear. These compressive forces will have resultants opposing the motion of the fluid so that the viscous drag of the particle will be greater than would be the case in the absence of the cloud. Fig.

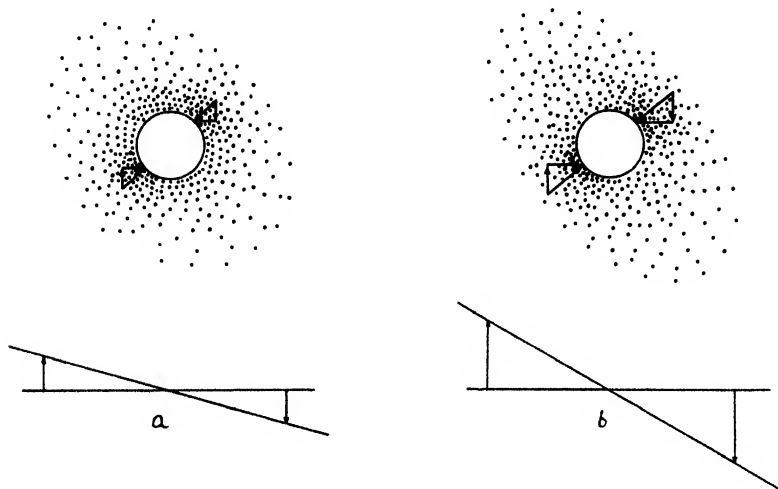


FIG. 9

A lyophilic particle under low and high shear showing how the cyboma cloud opposes the motion of the fluid.

9, b, shows the effect of a high rate of shear. It is hardly to be expected that the opposing force due to the distortion of the cloud will be a linear function of the rate of shear, but it seems probable that it will go through a maximum at high shearing rates. Compliance of a colloidal solution of type (2) or (3) with Newton's Law of the constancy of viscosity with rate of shear can, therefore, not be expected. The deviations will most likely be much greater with colloids of the third type. Again in this case the effect will be more pronounced with small particles than with large.

The influence on viscosity just described will be independent of the existence of other particles in the solution. There is yet another influence on viscosity due to the proximity of the micelles and which will doubtless have the greatest effect in concentrated sols. As two particles pass each other in a sol under shear, the clouds surrounding each will interpenetrate and produce repulsions which can greatly increase the viscous drag, both due to the parallel components of the forces and to the fact that the particles will describe lengthened paths around each other. Fig. 10, a, represents schematically the interactions of two particles as they approach at low rate of shear. It will be re-

membered, from what has been said earlier, that the repelling force will depend upon disturbance of the equilibrium at the surface of a particle and, therefore, there will be a lapse of time between the penetration of the outer parts of the clouds and the development of the repulsion. The work required to move one particle past the other at a given distance will, therefore, diminish with increasing velocity of the particle. In addition, the extent of the cloud in the direction of the other particle will be reduced by rate of shear as shown in Fig. 10, b, so that at high rates of shear, the particles can approach much closer to each other, and they will be more nearly opposite before experiencing

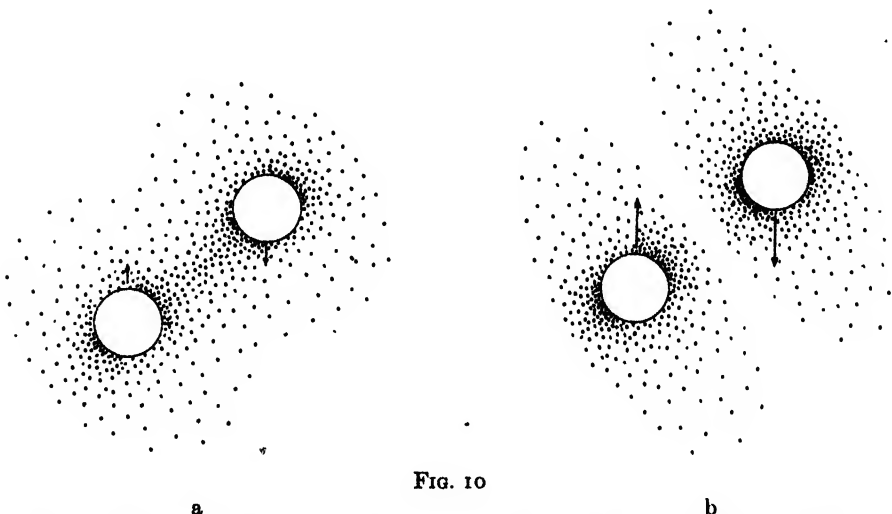


FIG. 10

Two lyophilic particles passing at low and high shearing rates. The effect of rate of shear upon the mutual interference of the particles is clearly seen.

repulsion, so that the viscous drag will be much less at high shearing rates than at low. This difference in affect of rate of shear can be easily seen by comparing Figs. 10, a and b.

It might be assumed that as the particles pass each other at high shear and the distorted clouds intermingle there will be a repulsive force which will contribute to their progress and thus tend to decrease the viscous drag. Fig. 11 shows such a case. However, upon more careful consideration of the conditions existing in Fig. 11, it is evident that these distorted sections of the clouds intermingling are being swept away from the particles so that, although there will be a region of greater density of the cybomas between the micelles, the time lag previously mentioned will prevent any appreciable concentration effect at the micelle surfaces before they are swept out of range.

As would be gathered from examination of Figs. 5 and 6, this viscous effect depending on the proximity of the particles should increase rapidly with increasing concentration, and also at constant concentration should increase with decreasing particle size. The latter effect being due to the much smaller average distances between the small particles.

From what has gone before it is to be concluded that a decrease in particle size will inevitably lead to an increase in viscosity in all solutions of type (3), and probably also of type (2) since the interactions of the particles will probably play a more important rôle than the effect on the total number of cybomas in the liquid. Experimental results such as those of Odén¹⁴ on sulphur sols lend support to this prediction.

Double Refraction of Non-Spherical Particles

From general considerations it would be predicted that the optical axis of non-spherical particles suspended in a liquid under shear would coincide

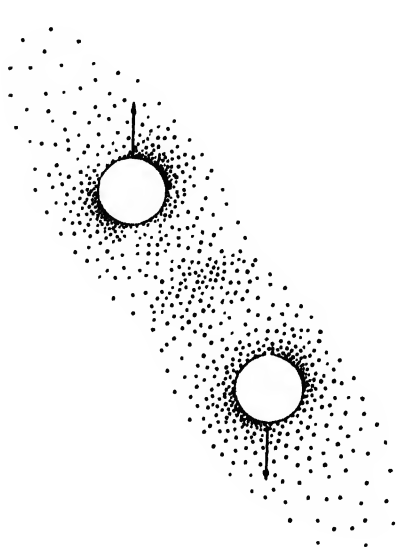


FIG. 11

Conditions existing after two particles under shear have passed.

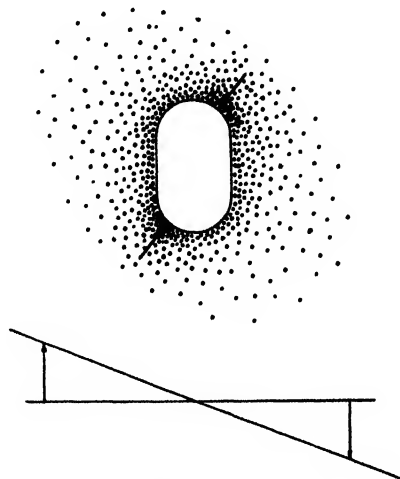


FIG. 12

Illustration of the unbalanced forces acting on an elongated particle lying in the plane of shear. The necessity for rotation of the axis out of the plane of shear is shown.

with the plane of shear, but this has been found to be the case only with coarse dispersions. In most cases that have been investigated the axis lies at an angle between 0 and 45° with the plane. With elastic solids and jellies the angle is 45°. There has been no adequate explanation of the failure of the particles to orientate themselves completely in the plane of shear and statements such as the following from Kraemer¹⁵ have received widespread if tentative acceptance. "The particles in the sols mentioned seem to be united in some way, forming a more or less tenuous, elastic structure that undergoes deformation as well as orientation."

An orientation of non-spherical particles at an angle with the plane of shear arises out of necessity from our hypothesis of the conditions surrounding

¹⁴ Z. physik. Chem., **80**, 709 (1912).

¹⁵ Kraemer: "Treatise on Physical Chemistry," Edited by Hugh S. Taylor, **2**, 1609 (1931).

(The first person to postulate this connection between orientation and elastic deformation seems to have been Pontremoli: Atti Accad. Lincei, **30** II, 216 (1921).)

a particle of type (2) or (3). Referring to Fig. 9, a or b, one will immediately see that in case the particle is elongated, the forces acting upon it from opposite sides will no longer be balanced and there will be a rotation of the particle to a new position at an angle with the stream. This unbalanced condition can more readily be visualized by reference to Fig. 12. The particle will rotate in a direction away from the approaching current and the extent of rotation will be less the more elongated the particle is. With increasing rate of shear the angle of deviation should be reduced since the viscous drag on the surface is in such a direction as to oppose the orientating forces.

Freundlich, Neukircher, and Zocher¹⁶ have carefully measured the optic axis of several non-spherical sols and their results confirm completely the predictions made above. For example, the angle is found to decrease with age of a vanadium pentoxide sol, while the length of the particle increases. The angle decreases with increasing rate of shear and its direction with respect to the motion of the liquid is what has been predicted. While their offered explanation based on the existence of swarms of micelles can in no way be said to be invalidated, certainly the explanation based on the influence of the cymomas seems to involve less artificiality.

It does not longer seem to be necessary to postulate the existence of elastic forces acting at relatively great distances throughout the sols.

Thixotropy

In sols of type (3), it is evident that particles will tend to take up positions at maximum distances from each other, which means that barring other disturbances, a quiet sol will assume a definite structure. Any small force tending to destroy this structure will be met by a quasi-elastic resistance, and if the disturbing force is quickly enough withdrawn, there will be elastic recovery from the deformation. Such elastic resistance must be met due to the fact that when the micelles are in the configuration of maximum distance from each other, any small deformation must reduce this distance, thus increasing the forces between certain of the micelles in a direction which would oppose the disturbance.

Even in the absence of Brownian movement, the opposing force, induced by a small deformation, would gradually sink to zero due to the migration of the particles to new optimum positions, a phenomenon which resembles closely in external aspects relaxation under stress in elastic solids.

The presence of Brownian movement will naturally hinder the complete orientation of the micelles into optimum positions, so that the higher the temperature, other things being equal, the less distinctly will the elastic properties manifest themselves. Since the repelling forces between particles rise rapidly with increase in concentration, a concentrated sol may show a definite yield point, whereas a more dilute sol may be sufficiently disturbed by Brownian movement so that no yield value can be obtained even at very low rates of shear. In the more concentrated sol, the shearing stress will approach a con-

¹⁶ Kolloid-Z., 38, 43, 48 (1926).

stant value with decreasing rate of shear as shown by Curve 1, Fig. 13, while in the dilute sol, due to the rapid relaxing affect of the Brownian motion, no limiting value of shearing stress will be approached but as the rate of shear becomes very small, the shearing stress will drop off in the manner of Curve 2, Fig. 13. These two curves will be recognized to be very typical of lyophilic colloidal solutions.

Again decrease in particle size will manifest itself in a direction similar to increase in concentration, since, although Brownian disturbances will increase with decreasing particle size, the inter-micellar forces will increase more rapidly.

The influence of concentration upon the yield point cannot be exactly given, but in the simplified case where Brownian movement is assumed to be negligible, it seems justifiable to assume that each particle is surrounded by practically a sphere of other particles, i.e., it is circumscribed by a spherical envelope where $dn'/dr = 0$, the conditions assumed for Figs. 5 and 6. The yield point of the sol should therefore be approximately proportional to dP'/dR , since the restoring forces after a disturbance will be proportional to the same quantity. Taking R as proportional to the cube root of the volume, the variation of yield point with volume of sol should be somewhat as shown in Fig. 14 for particles of 100 Å radius. From this figure one would certainly anticipate evidence of yield point in sols of small particle size when the volume of colloid is greater than 10% of the total volume.

Due to the time required for the forces to produce optimum orientation, a lyophilic sol that has been thoroughly mixed will show a rise in viscosity with time. On the other hand, if the sol is allowed to stand quiescent in a viscometer and then its viscosity is measured at constant rate of shear, it will be found to decrease with time and extent of working to some constant value which, however, will be smaller the greater the rate of shear, due to the smaller opportunity for the repelling forces to set up the ordered arrangement.

This rise in viscosity with quiescence and return again upon working, particularly when the sol develops a definite yield value upon standing, has been termed thixotropy. Several tentative explanations have been proposed for it but none have been found satisfactory, and it was in a search for a satisfactory explanation that the author was led to a consideration of the influence of cybotactic complexes.¹⁷

Although the explanation as given seems to account successfully for numerous observations, it does not seem to me that the yield value described above

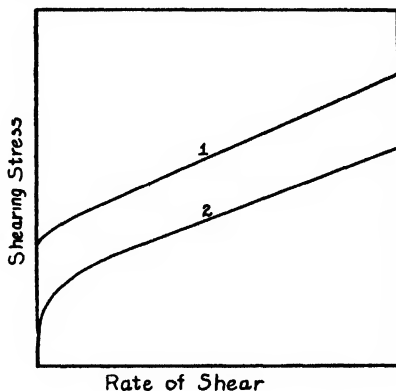


FIG. 13

Typical stress-rate of shear curves for sols. Curve 1 shows a definite yield point while 2 shows none.

¹⁷ Kistler: J. Phys. Chem., 35, 828 (1931).

can have the magnitude of that found in certain thixotropic gels, such as those of Fe_2O_3 and Al_2O_3 . In these cases, probably reversible coagulation plays a part. These gels belong to the class in which a decided Zeta potential is necessary for stability, and it may be that upon the addition of the small amount of electrolyte necessary to bring about the thixotropic condition, the surface is changed to type (2) in which there is a definite attraction between particles. Since this attractive force undoubtedly extends farther than the electric repulsion there will be a tendency for the particles to take up positions with respect to each other at a smaller distance than the average distance of separa-

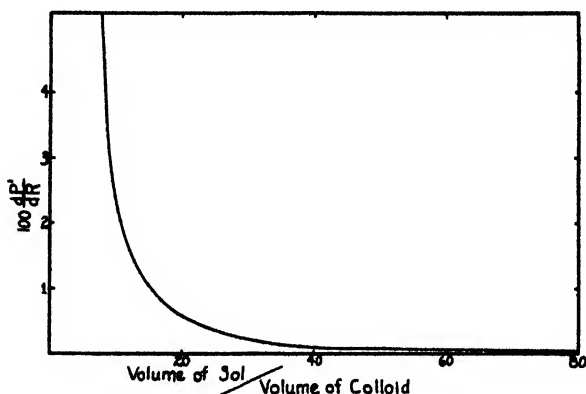


FIG. 14

Curve illustrating the probable influence of the dilution of a lyophilic sol upon the yield point.

tion of the particle in the sol. Under such circumstances the particles in a quiescent sol will tend to collect into flocks which may be irregular and tenuous. Within each swarm of micelles the particles would tend to assume very definite positions with respect to each other in which the attractive forces would be counter balanced by the electric repulsions. Since the average distance separating the particles in any one swarm would probably be small due to the limited extent of the electric fields, the swarm could possess considerable rigidity. Since the micelles forming any swarm must be drawn from the liquid in the immediate neighborhood, the swarms must necessarily be small in cross section but may be inter-connected so that they form in effect an anastomosing sponge-like structure extending throughout the whole volume of the sol. Such a structure when completely formed could give the sol a rigidity much greater than it could possess if the particles remained dispersed at maximum distances. This two-phase sol would assume the aspects of a gel but would again become a mobile liquid upon mechanical agitation and dispersion of the swarms.

If the above explanation of this particular type of thixotropic sols is correct, one would expect that the thixotropic condition would occur only in a very limited range of electrolyte concentration. Occurring as a balanced condition between electric charge and attractive force one should expect that only cer-

tain sols would be capable of attaining this balance. In general, the sols of type (2) would coagulate rather than halt on this metastable plateau. These expectations have been realized and although it may become possible to induce thixotropy in many more sols, at present the number of electrolyte-sensitive sols that have been brought into this condition is relatively small.

Such swarms of particles as have been postulated above have been demonstrated to exist in aged V_2O_5 and Fe_2O_3 sols.¹⁸ Zocher has applied the term "tacto-sols" to these swarms. Those that he has studied have shown a definite optic axis which indicates that the particles are non-spherical and orientated. The orientation, there observed, would be a natural consequence of formation as above postulated.

Although the theory of the influence of cybotactic complexes upon colloidal systems as presented above, offers, in itself, an explanation of a large number of phenomena, I do not wish to imply that it is the sole cause of these phenomena, but that it is a general background upon which may be superimposed other effects which have been given credence in the current literature.

It is a pleasure to acknowledge my indebtedness to Dr. David G. Bourgin, Mathematic Department, University of Illinois, for his assistance in deriving and checking the formulas used, and to Professor H. Freundlich, Berlin, for carefully reviewing the manuscript before its presentation.

Summary

1. The existence of cybotactic complexes in liquids is discussed and it is shown that colloids may be divided roughly into two classes, corresponding to lyophobes and lyophiles, depending upon whether the surfaces tend to depress or stimulate the formation of cybotactic complexes, called here "cybomas."
2. The stability of a lyophilic sol is shown to depend mainly upon a concentration gradient of cybomas decreasing with distance from each colloid particle, while the tendency to coagulate and the previously postulated force of unknown origin tending to draw particles at a distance together in lyophobic sols are connected with a gradient of opposite sign.
3. Reasonable assumptions are made in regard to the average size and average life of cybomas, and equations derived showing the relatively great distance into a liquid at which a surface may have influence.
4. The differences between ease of dispersion of lyophile and lyophobe colloids, and the unexpectedly large rate of diffusion of the former are explained.
5. An explanation of the lyotropic series $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow NH_4^+$ is given.
6. The fact that lyophilic sols tend to possess very uniform particle size is predicted from the interactions with cybomas.
7. The tendency shown by lyophiles to precipitate in fibriles, plates or "brush heaps" enclosing much liquid is shown to be a necessary consequence of the assumptions made.

¹⁸ Zocher: *Z. anorg. Chem.*, **147**, 91 (1925); Zocher and Jacobson: *Kolloid-Z.*, **41**, 220 (1927); *Kolloidchem. Beihefte*, **28**, 167 (1929).

8. A probable influence of cybomas on the tendency of large hydrated molecules such as sucrose to supersaturate is indicated.

9. The influence of a colloid on the viscosity of a liquid is ascribed to three separate affects, (a) the influence on the total number of cybotactic complexes, (b) the interaction between these complexes and a particle under shear, tending to increase the resistance offered by the particle to viscous flow, and (c) the interactions between two particles while passing, due to intermingling of their attendant cyboma swarms. It is pointed out that the particle size of lyophiles must have a large influence on viscosity, the smaller the particles the greater the viscosity.

10. The fact that nonspherical particles do not orient themselves in the plane of shear is shown to arise of necessity from the adopted assumptions, and the direction of rotation as well as the influence of rate of shear and particle size are predicted.

11. The failure of a lyophilic sol to show constant viscosity with different rates of shear, the rise in viscosity with decrease in shearing rate, the decrease of viscosity with time at constant rate of shear, and the existence of a yield point are predicted. In other words, thixotropy is given a rational explanation.

12. A reasonable explanation is offered for Zocher's "tacto-sols."

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THE ADSORPTION OF ELECTROLYTES BY ASH-FREE CHARCOAL

VII. A Brief Survey of the Present Status of the Subject, and Evidence that Negative Adsorption of Inorganic Bases decreases with Length of Time of Contact of Charcoal with Solution*

BY ELROY J. MILLER

At the Fifth Colloid Symposium¹ a summary was presented of the studies that had been carried out on adsorption from solutions of acids, bases and salts by adsorbent charcoal. It was pointed out that the earlier results obtained by Freundlich, Michaelis, Odén, and others in their adsorption studies with blood charcoal were anomalous and contradictory. In the light of the results obtained with activated sugar charcoal and other ash-free charcoals, these discordant results could be satisfactorily explained on the basis of impurities in the charcoal such as ash, incompletely decomposed organic matter, and unsuspected adsorbed acids. The results with the ash-free sugar charcoal, and with the purified charcoals of animal and vegetable origin, were surprisingly consistent and reproducible, and many new facts were established which since that time have been verified in a number of laboratories. Adsorption from solutions of electrolytes seemed to be on a firm basis and the groundwork was indeed laid for many future investigations, as is evidenced by the scores of papers that have appeared on the subject since that time. It seems desirable again to present a brief survey of the present status of the subject.

It will be recalled that ash-free adsorbent charcoal that has been heated at temperatures around 1000° has the property of adsorbing acids, but it does not adsorb the inorganic bases.² From many salt solutions the charcoal adsorbs acid hydrolytically with the liberation of alkali. Ash-free charcoal adsorbs large amounts of acids such as benzoic and salicylic. Dicarboxylic acids such as succinic, malic and tartaric are moderately adsorbed. Adsorption of aliphatic acids increases with increasing length of carbon chain. Inorganic acids, such as HCl, H₂SO₄ and HNO₃, are relatively slightly adsorbed. Inorganic bases are not adsorbed at all. The introduction of polar groups such as hydroxyl and amino groups into organic acids decreases adsorption. In the aliphatic acid series the shorter the carbon chain the greater is the effect of the introduction of the polar groups. Thus the introduction of the amino group into acetic acid cuts down the adsorption completely. Furthermore, the position of the polar groups in the molecule influences the adsorbability of the acid. O-, m- and p-hydroxy benzoic acids and o-, m- and p-amino benzoic acids are adsorbed in different amounts depending upon the position of their polar groups; the ortho acid is adsorbed most, the para next and the meta least. Isomeric forms of the fatty acids, butyric, valeric and caproic are adsorbed less

* Contribution from the Chemical Laboratory of the Michigan Agricultural Experiment Station. Published with the permission of the Director of the Experiment Station as Journal Article No. 122 (n.s.)

than the normal forms. It should be particularly noted that while NH_4OH is not adsorbed at all, tetramethylammonium hydroxide is slightly adsorbed and tetraethylammonium hydroxide is quite appreciably adsorbed. It is interesting and significant that these organic bases which are practically as strong bases as are NaOH and KOH are positively adsorbed, whereas the latter are not adsorbed at all or are actually negatively adsorbed.

Complete Proof of Hydrolytic Adsorption

Methods were developed for the quantitative estimation of adsorbed acids on ash-free charcoal.³ Known amounts of acids were adsorbed on charcoal and the amounts of acid recovered were quantitatively equal to the amounts adsorbed for various types such as aromatic, dicarboxylic, aliphatic and inorganic acids. With the development of these methods for the quantitative estimation of adsorbed acids on charcoal it became possible to furnish complete proof of hydrolytic adsorption. The amount of alkali set free by the charcoal was determined and the charcoals were then examined for the presence of adsorbed acids. The results with salts of a number of organic acids showed that the amount of adsorbed acid recovered from the charcoal was exactly equivalent to the alkali set free and left in solution. Similar results were obtained with salts of inorganic acids, but in addition, the chloride and sulphate were determined and also found to be equivalent in amount to the acid adsorbed and base set free. Complete proof of hydrolytic adsorption from salt solutions was thus established. The charcoal contained no alkaline impurities, and the acid recovered from the charcoal was the same as that from which the original salt had been derived.

Hydrolytic and Molecular Adsorption from Salt Solutions

From an investigation of adsorption from a series of potassium salts⁴ it was found that the hydrolytic adsorption from solutions of inorganic salts was exclusively hydrolytic, while from salts of organic acids, adsorption was both hydrolytic and molecular. The concentration of potassium after adsorption had decreased in solutions of salts such as potassium benzoate and salicylate, indicating that besides hydrolytic adsorption of acid from the salt, there was adsorption of the salt as such. The concentrations of potassium in solutions of potassium sulphate, nitrate, and chloride were actually slightly higher after adsorption, indicating that only acid (and some water) was adsorbed from these solutions. It was evident from other facts that the increase in concentration was undoubtedly due to adsorption of water along with the acid hydrolytically adsorbed. It was observed that while the adsorption of the inorganic salts was exclusively hydrolytic the absolute amount of potassium hydroxide set free was approximately only one-fourth that set free from sodium benzoate.

Negative Adsorption of Potassium Hydroxide

By the use of larger quantities of charcoal (10 grams or more) it was definitely established⁴ that negative adsorption of potassium hydroxide occurs.

The concentration of potassium after adsorption was higher than in the original solution, but the absolute amount of potassium was the same before and after adsorption. These results on negative adsorption were all obtained under uniform conditions. The charcoal was always freshly ignited just before use and allowed to remain in contact with the solution for a definite length of time. It was found, however, that when these conditions were varied the resultant effects were not always in agreement.

Decrease of Negative Adsorption with Time

It was surprising to find (Table I) that the length of time the charcoal and solution remained in contact determined very largely the magnitude of the negative adsorption. And still more surprising was the fact that the magnitude of the negative adsorption, contrary to positive adsorption, decreased

TABLE I

Decrease of Negative Adsorption of NaOH with Time
14 g. Ash-Free Blood Charcoal (Old Type, 1925)
added to 100 cc. 0.02 N NaOH

Duration of Contact	Cc. 0.02 NaOH Adsorbed
5 minutes	-1.9
20 "	-1.4
35 "	-0.6
3 hours	+0.3
48 "	+1.8

9 g. Ash-Free Blood Charcoal (Old Type, 1929)
added to 100 cc. 0.02 N NaOH

30 minutes	-3.00
30 "	-3.52
25 hours	-0.60
70 "	-0.60

9 g. Ash-Free Blood Charcoal (Old Type, 1930)
added to 100 cc. 0.02 N NaOH

20 minutes	-2.30 (2)
20 "	-2.30 (4)
75 "	-2.90 (1)
43 hours	-0.10 (5)
53 "	-0.30 (3)

with time, and fairly rapidly. Thus in one experiment, at the end of thirty minutes 3 cc. of water had been adsorbed while at the end of twenty-six hours the value had decreased to 0.6 cc. In another experiment, at the end of fifteen minutes 2.9 cc. of water had been adsorbed and at the end of twenty-six hours the value had decreased to 0.1 cc. The results were somewhat erratic, however, and it was evident that not all the controlling factors were known. From

a considerable number of experiments (Fig. 1), however, it was quite evident that negative adsorption does decrease with time. When the adsorption effects were measured within thirty minutes after addition of the charcoal to solution, a considerably higher value for the water adsorption was obtained than when charcoal and solution remained in contact for a period of twenty-four to seventy hours. In a few instances positive adsorption appeared to be indicated, but it was later found that these were undoubtedly due to the fact that the temperature of ignition was too low, and substances of an acid nature had been formed on the charcoal.

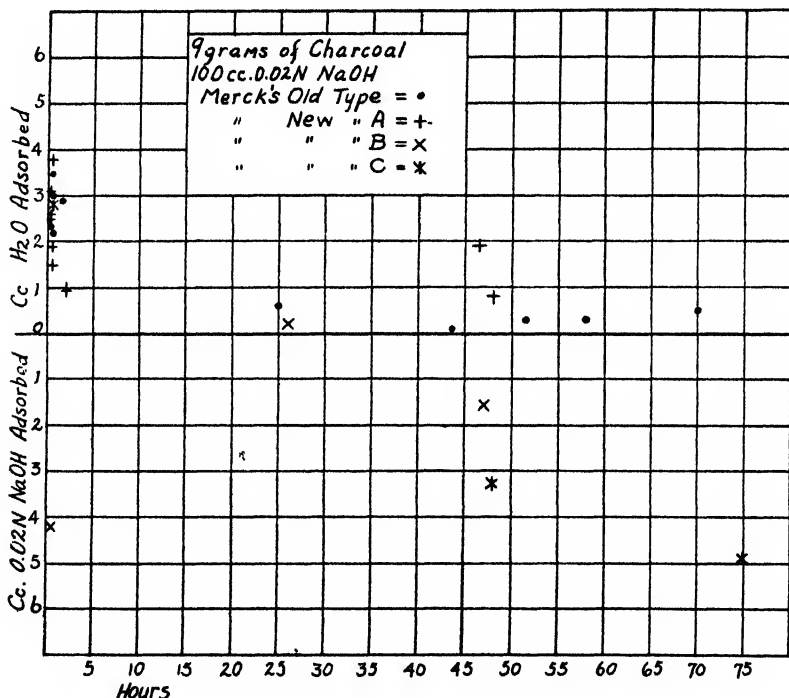


TABLE II

Effect of Temperature of Ignition of Charcoal on Adsorption of NaOH
9 g. Ash-Free Blood Charcoal (New Type) added to 100 cc. 0.02 N NaOH

Charcoal Sample	Temperature of Ignition	Duration of Contact	Cc. 0.02 N NaOH Adsorbed
No. 1	900°	30 minutes	+1.76
"	900°	30 "	+0.20
"	900°	30 "	-0.40
No. 2	900°	24 hours	+7.96
"	900°	30 minutes	+0.56
No. 3	900°	72 hours	+1.86
"	900°	30 minutes	+0.80
No. 4	1075°-1200°	2 hours	-0.96
"	1075°-1200°	30 minutes	-1.96
"	500°	20 "	+8.00
"	1200°	20 "	-3.10
"	500°	15 "	-2.60
"	1200°	47 hours	-1.90
"	1200°	20 minutes	-2.50
"	1200°	48 hours	-0.80

tion while the first heating gave a positive adsorption could not easily be explained at first, but Kruyt and de Kadt⁵ published a note somewhat later which afforded a simple explanation for the apparent discrepancy. They found that charcoal which had been heated at 900° and which adsorbed acids but not inorganic bases was reheated at 400° in oxygen, it acquired the property of adsorbing bases. This property could be destroyed by again heating at the higher temperature.

Kruyt and de Kadt postulated the formation of substances of an acid nature such as intermediate products of mellitic acid on the surface of the charcoal by the heating in oxygen at lower temperatures. At the higher temperature the acid substances were destroyed. These acids could easily account for the apparent adsorption of bases as had been repeatedly shown¹ for adsorbed acids on ash-free charcoal. For example, an ash-free charcoal heated at 1075° adsorbed a large amount of benzoic acid but no sodium hydroxide. When complex water-insoluble methyl red acid was adsorbed on the charcoal it was able to take up a considerable amount of alkali (molecular adsorption of salt of strongly adsorbed organic acid), and when the charcoal was reheated at 1075° to destroy the methyl red acid, the charcoal no longer took up any alkali, but still adsorbed benzoic acid. Kruyt's charcoal and charcoal carrying adsorbed organic acids then have properties in common.

The apparent discrepancies in the behavior of the charcoal after various heat treatments were eliminated when it was found necessary to heat the charcoal above 900° for a considerable time in order to completely decompose the acid formed on the charcoal. Once the charcoal has been freed from the carbon acids, however, heating at 500° in the absence of air does not result in

the formation of the acid, and negative adsorption of alkalis which decreases with time is still observed. For rapid formation of the complex acid it is necessary to heat the charcoal at 300-400° in the presence of air and water vapor, although the action takes place slowly even at room temperature.

Recently, Kolthoff⁶ has attempted to obtain more information on the nature of the acid formed on the surface of Kruyt's charcoal and found evidence of the formation of a complex colloidal acid. If taking up of alkali by Kruyt's charcoal is the same as adsorption of acid, then the 400° charcoal should adsorb KOH hydrolytically from KCl with the liberation of HCl, but Kolthoff could not detect any liberation of HCl and indeed the chloride content of the solution after adsorption had decreased slightly. The solution had become slightly acid, however, and Kolthoff found some evidence of the presence of a complex colloidal acid.

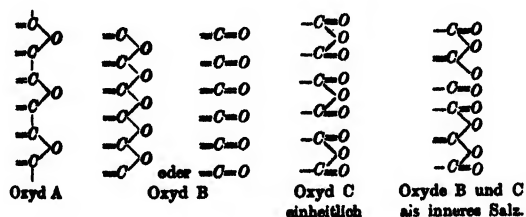


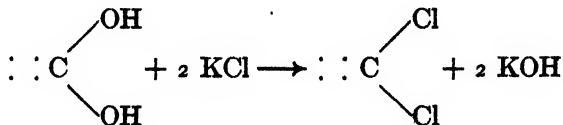
FIG. 2

Schilow's Oxides of Carbon

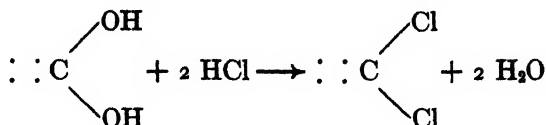
Schilow's Oxide Theory

About the time that Kruyt and de Kadt made their discovery, Schilow and co-workers⁷ also observed that charcoals heated at lower temperatures took up bases. From this and other facts they postulated a theory that adsorption of acids, bases and salts by charcoal takes place through interaction with acidic and basic oxides of carbon on its surface. Schilow⁸ pictures these oxides (Fig. 2) as A which with water gives a slightly basic carbon hydroxide, oxide B which forms a strongly basic hydroxide and oxide C which is acidic in nature. An inner salt of oxide B and C is also pictured. Oxide A is stable at all temperatures and in presence of oxygen up to 2 mm. pressure. Oxide B is formed from A at 2 mm. oxygen pressure and is stable up to very high pressures. Oxide C is formed from oxide B by heating in oxygen at 300-700°.

Schilow's explanation of the mechanism of hydrolytic adsorption is as follows:



The chloride ion of the KCl replaces the OH ions and KOH remains in solution. Hydrochloric acid would of course react with oxide B to leave water in place of KOH, while potassium hydroxide would not react at all with it.



Schilow⁹ found also that the oxygen pressure on the charcoal influenced markedly the adsorption of hydrochloric acid. In Fig. 3 are his curves for the adsorption of hydrochloric acid in a number of concentrations as affected by the oxygen pressures. The action is stepwise and independent of the adsorption isotherm for oxygen. At pressures up to 2 mm. the curves are horizontal,

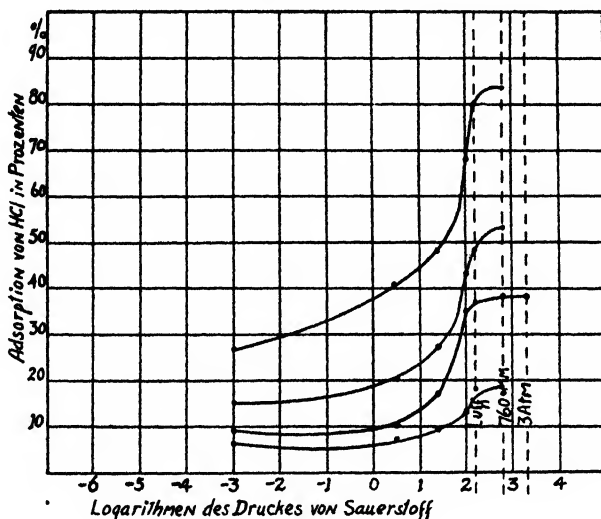


FIG. 3

Schilow's Curves for Adsorption of HCl against Oxygen Pressures

then there is a sharp break followed by another horizontal section. The lower section represents the adsorption by oxide A and the steep part marks the formation of oxide B, and the second flat part the adsorption by oxide B.

Frumkin's Gas Electrode Theory

Frumkin and co-workers,¹⁰ however, obtained entirely different results for the relation between oxygen adsorbed and hydrochloric acid adsorbed. They found that within certain limits the milliequivalents of hydrochloric acid adsorbed were equal to the milliequivalents of oxygen adsorbed. Their curve for oxygen adsorption (Fig. 4) against pressure was smooth, and the adsorption of HCl was equivalent to the oxygen taken up (Table III). They have an entirely different explanation for the adsorption of acids, bases and salts.¹¹ Their theory is essentially that activated charcoal in the presence of hydrogen or oxygen functions as a gas electrode. In the presence of oxygen, hydroxyl ions appear in solution and the positive charge on the charcoal then attracts anions and adsorbs acids but not alkali. Neutral salts are hydrolytically ad-

TABLE III

Milliequivalents of Oxygen per g. Charcoal	Milliequivalents HCl Adsorbed per g Charcoal
0.012	0.012
0.033	0.035
0.044	0.043
0.052	0.051

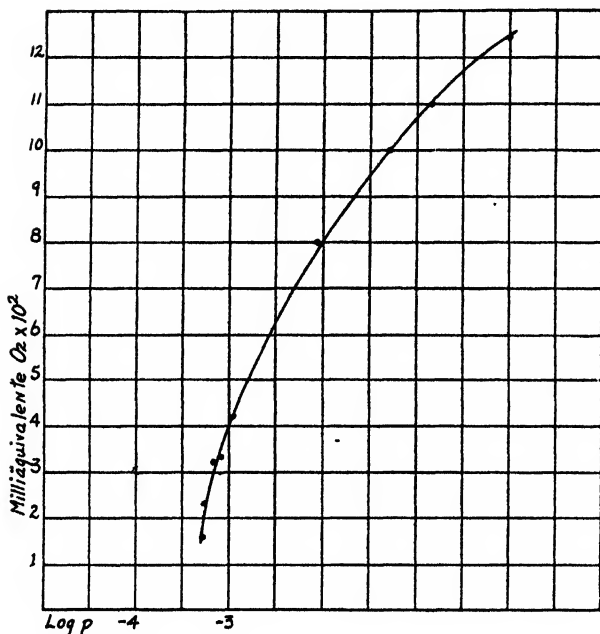


FIG. 4

Frumkin's Curve for Adsorption of Oxygen at Different Pressures

sorbed with the liberation of alkali. In an atmosphere of hydrogen, hydrogen ions appear in solution, leaving the charcoal negatively charged and in a position to attract cations. Alkali is adsorbed but not acid. Neutral salts are hydrolytically adsorbed with the liberation of acid.

Frumkin's early experiments¹¹ with charcoal alone did not entirely support his theory, but when platinum was incorporated with the charcoal the adsorption of HCl and NaOH in atmospheres of hydrogen and air was in keeping with the theory (Table IV). HCl was adsorbed in the presence of air but not in hydrogen, while NaOH was not adsorbed in air but was adsorbed in hydrogen. Through improvement in technique, however, Frumkin¹² was able to show (Table V) that charcoal even in the absence of platinum behaved in keeping with the theory, and that from potassium chloride in an atmosphere of hydrogen KOH was hydrolytically adsorbed, while in air HCl was taken up. Hydrochloric acid was not adsorbed in hydrogen but was adsorbed in air.

TABLE IV

Per cent Pt.	Milliequivalents HCl adsorbed in Presence of		Milliequivalents NaOH adsorbed in Presence of	
	Air	Hydrogen	Air	Hydrogen
0.00	0.227	0.190	0.000	0.000
0.004	0.298	0.116	0.000	0.000
0.032	0.333	0.048	0.000	0.426
0.16	0.358	0.000	0.000	0.521
0.80	0.376	0.000	0.000	0.557
4.00	0.393	0.000	0.000	0.576
10.00	0.406	0.000	0.000	0.582

TABLE V

	Charcoal saturated with H ₂ adsorbs KOH KCl Solution	Charcoal saturated with Air adsorbs HCl
I	0.0216	0.025
II	0.021	0.025
III	0.0205	
	Charcoal saturated with H ₂ adsorbs HCl HCl Solution	Charcoal in Presence of Air adsorbs HCl
IV	0.0	0.14
V	0.0	0.139
VI	0.0	
	Charcoal saturated with H ₂ adsorbs KOH KOH Solution	Charcoal in presence of Air adsorbs KOH
VII	0.66	0.0
VIII	0.0655	0.0

TABLE VI

Amount of HCl adsorbed Millimoles		Amount of NaOH adsorbed	
In vacuo	After contact of Charcoal with air	In vacuo	After contact of Charcoal with air
0	0.140	0	0
0	0.140	0	0

Potassium hydroxide was adsorbed in hydrogen but not in air. Frumkin¹³ was finally able to demonstrate (Table VI) that in a vacuum, in the absence of both hydrogen and oxygen, neither acid nor alkali was adsorbed. Schilow,¹⁴ however, always maintained that even in vacuo the charcoal adsorbed hydrochloric acid through the agency of his oxide A which was stable even at low pressures and high temperatures, and that KCl was not hydrolytically adsorbed by this oxide. Frumkin¹⁵ questioned Schilow's results and pointed out

that it is necessary to continue the heating of the charcoal for twenty-four hours in a high vacuum in order to get rid of all the oxygen. But at the same time with improved technique Frumkin found that the hydrogen atmosphere no longer prevented the adsorption of hydrochloric acid when the concentration of the acid solution was above 0.1 Normal. In concentrations above tenth-normal the adsorption increased rapidly in spite of the presence of hydrogen. This Frumkin attributed to molecular adsorption.

Recently Bretschneider,¹⁶ working in Ruff's laboratory, has reported that the adsorption of succinic acid in air and in vacuo is the same (Table VI). This substantiates Frumkin's findings¹¹ that the adsorption of benzoic acid is not

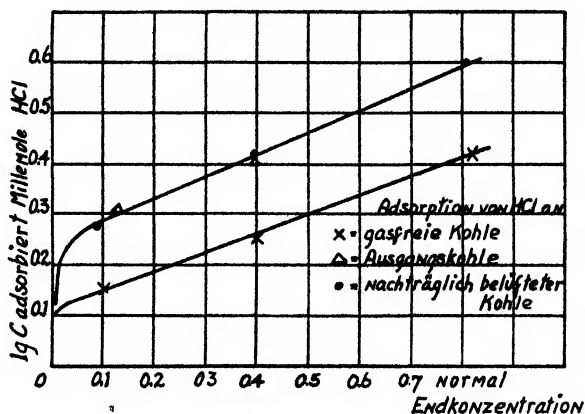


FIG. 5

Bretschneider's Curves for Adsorption of HCl

influenced by the presence of hydrogen or oxygen, even by platinized charcoal. Contrary to Frumkin, Bretschneider found that hydrochloric acid is quite appreciably adsorbed by charcoal in vacuo but in the presence of air the adsorption is increased, practically to the same value for the original charcoal in air. From Bretschneider's curves (Fig. 5) it is apparent that the original charcoal and the evacuated charcoal to which air had afterward been admitted had identical adsorption capacities. The practically constant difference between the values for evacuated charcoal and charcoal in air Bretschneider attributed to the presence of Schilow's oxide B which can bind hydrochloric but not succinic acid. He favors Schilow's theory and states that Frumkin's theory does not afford any better explanation.

Discussion

In view of the uncertain and controversial status of much of the evidence for the oxide and gas electrode theories it is difficult, if not impossible, to evaluate them at present. One thing, however, appears to be certain, and that is the section of the field of adsorption of electrolytes from solution to which they apply is very limited. Frumkin and Schilow have both recognized this fact and emphasize that molecular adsorption is not excluded by their theories.

It should be pointed out that, on the whole, the experimental evidence indicates that only those substances which are least adsorbed or not adsorbed at all in the presence of air are influenced by the nature of the gas adsorbed on the charcoal, and these only in lower concentrations. The adsorption of HCl from dilute solutions by charcoal apparently can, under certain conditions, be influenced by the presence of hydrogen, but in higher concentrations it is not affected. Only the first two or three members of the aliphatic acids,¹⁷ which are relatively slightly adsorbed, are appreciably influenced, but the effect falls off rapidly with increase in length of carbon chain. The more strongly adsorbed organic acids such as benzoic and succinic are not affected by the adsorbed gas. The reason for this, Frumkin¹¹ states, is that acids such as benzoic are like non-electrolytes in their adsorption by charcoal. This explanation encounters serious difficulties when the adsorption behavior of bases is considered.

It is difficult to explain, by either of the theories, why sodium and potassium hydroxides are not adsorbed in the presence of air, while the equally strongly dissociated organic base, tetraethylammonium hydroxide is adsorbed; and again, on the other hand, the weak base, ammonium hydroxide, is not adsorbed. Equally difficult to understand is the fact that the adsorption of KCl, which is exclusively hydrolytic, can be affected by the gaseous atmosphere, while the greater hydrolytic adsorption of potassium benzoate is not affected. Under the circumstances it would be necessary to account for hydrolytic adsorption of potassium chloride by one theory, and hydrolytic adsorption of potassium benzoate by another. The effect of introduction of polar groups on adsorption does not seem to be explainable by either of the theories, nor is the negative adsorption of sodium and potassium hydroxides and its decrease with length of time of contact of charcoal with solution.

Roychoudhury and Mukherjee¹⁸ have put forth the argument against the gas electrode theory that Kruyt's charcoal in oxygen is negatively charged whereas charcoal in oxygen according to Frumkin's theory should be positively charged. If, however, Kruyt's charcoal does contain carbon acids with the carboxyl groups extending into the water phase, the negative charge could arise from the dissociation of the COOH group. This is in keeping with the fact that this charcoal is easily wetted by water whereas the same charcoal heated to a high temperature is very difficult to wet. This charcoal after destruction of the carboxyl groups could, in oxygen, be positively charged according to Frumkin's scheme. It is clearly possible to have charcoal either positively or negatively charged in oxygen, depending upon the conditions of the previous heat treatment, and the argument, therefore, is not a valid one against the gas electrode theory. Furthermore, it seems possible that some of the experimental evidence and procedure employed by Roychoudhury¹⁹ are open to question. In the first place his charcoal was heated at 600° which is not high enough to destroy or drive off the acid products on the surface of the charcoal and they probably are even slowly formed at that temperature, for the optimum is in the neighborhood of 400°. As is evident from the data presented in this and previous papers it is necessary to heat the charcoal

around 1000° or above to free it from its acidic properties and to obtain a charcoal that does not take up alkali. Roychoudhury's charcoal, therefore, probably carried some acid products.

Another procedure which is open to question and which may have vitiated some of Roychoudhury's results is that of washing the charcoal with conductivity water to effect purification. In the early work with ash-free charcoal it was repeatedly pointed out^{1,20,21} that it is practically impossible to wash out easily measurable amounts of acid by repeated extraction with conductivity water alone. In Table VII are given the results of one experiment which illustrates this fact fairly well. Methods for the quantitative estimation of adsorbed acids on charcoal were developed,³ and procedures for detecting and measuring acidic and alkaline impurities were devised.²¹ In view of the results obtained with these methods it is exceedingly doubtful whether conductivity measurement as carried out by Roychoudhury is any indication of the quantity of acid adsorbed on the charcoal. How futile such a measurement is

TABLE VII

Removal of Adsorbed HCl from Charcoal by Extraction with Water
Each Extraction with 200 cc. Conductivity H₂O

Extraction No.	Period of Contact	Temp.	Acid Removed Cc. 0.02 N
1	15 hours	Room	0.00
2	1 "	Boiling	1.50
3	30 minutes	"	0.80
4	60 "	"	1.00
5	10 "	"	0.40
6	15 hours	Room	0.00
7	5 minutes	Boiling	0.19
8	1 hour	"	0.20
9	2 "	"	1.10
10	2 "	"	0.55
11	2 "	"	0.40
12	1 "	"	0.20
13	15 "	Room	0.00
14	10 minutes	Boiling	0.10
15	1 hour	"	0.15
16	1 "	"	0.20
17	8 "	"	0.30
18	1 "	"	0.20
Total HCl extracted by water.....			7.20
Extracted by boiling with NaOH			7.09
Acid recovered from charcoal equivalent to.....			14.29 cc. 0.02 N
Chloride " " " " "			14.19 " "
Acid originally adsorbed on charcoal.....			14.34 " "

as a means of detecting impurities on the charcoal can be judged from the fact that large quantities of acids can be irreversibly adsorbed on the charcoal, leaving no detectible amount of acid in solution. In fact the charcoal will even adsorb acid from a slightly alkaline solution of KCl ,⁴ and it requires more than one extraction with a considerable excess of alkali at boiling temperature to extract all the adsorbed acid. From the data in Table VII it is evident that equilibrium at room temperature left no acid in solution. At boiling temperature, however, there was an appreciable quantity in solution. The amount of acid removed with each extraction was dependent, not upon the length of time the charcoal was boiled, but upon the temperature at which it was filtered. In fact it is considerably more efficient to extract the acid by percolating boiling water through the charcoal, thus preventing the establishing of equilibrium. This, however, is not to be recommended as a reliable method for removing adsorbed acids, except possibly for removing the bulk of adsorbed acid from a small amount of charcoal. In the experiment summarized in Table VII, 14.34 cc. of 0.02 N HCl was (at room temperature) irreversibly adsorbed on 2.3 g. of charcoal. This furnishes some idea of the quantity of even a slightly adsorbed acid that can be adsorbed without leaving detectible amounts in solution.

That oxides do exist on the surface of the charcoal seems certain from the well-known fact that when oxygen is adsorbed on charcoal it is not recoverable as desorbed oxygen but as CO_2 at lower temperatures and as CO at higher temperatures, and that the heat of adsorption of small amounts of oxygen on charcoal is much higher than that of larger amounts. On the other hand, it is not so easy to determine definitely the form in which these oxides exist on the charcoal. Kruyt's idea of intermediate products of mellitic acid seems plausible, for his charcoal, as pointed out above, does have properties in common with charcoal carrying strongly adsorbed complex organic acids.

The idea of basic oxides of carbon does not seem so easily accepted in any case and it is rather difficult to understand why such a basic oxide as Schilow's B should react with HCl but not with benzoic or succinic acids¹⁶ when the fact is that the latter are much more strongly adsorbed by charcoal than is hydrochloric acid.

Additional evidence of the existence of acid oxides of carbon was discovered in the course of the study in this laboratory of methods for the quantitative removal of adsorbed acids from charcoal. An attempt was made to remove the acids by electrodialysis. The following results were obtained:

1. Charcoal heated at 1075°C . (not electrodialyzed) did not adsorb alkali.
2. Charcoal after electrodialysis did not adsorb alkali.
3. Adsorbed HCl was quantitatively removed by electrodialysis.
4. Charcoal from which adsorbed HCl had been removed by electrodialysis did adsorb alkali.
5. Carbon dioxide appeared in both anode and cathode chambers during electrodialysis.

While it was expected that the adsorbed hydrochloric acid would be removed by electrodialysis it was surprising to find that the charcoal after re-

removal of the acid was still able to take up alkali. This was quite contrary to the behavior of the charcoal after adsorbed hydrochloric acid had been removed by other methods. The appearance of relatively large quantities of CO_2 in both anode and cathode chambers during the process of removal of the acid was unexpected. Further investigation will have to be made to elucidate the factors involved, such as the nature of the electrode and membrane materials, and the voltage applied. It is not easy to explain the fact that the charcoal through adsorption and removal of HCl by electrodialysis should acquire the ability to take up alkali. These and many more perplexing facts must await further work before they can be satisfactorily explained.

Summary and Conclusions

1. A brief survey of recent trends and developments in studies on adsorption of electrolytes by ash-free charcoal has been presented.
2. Data have been presented which indicate that negative adsorption of alkali decreases with length of time the charcoal is in contact with the solution.
3. Data have been presented which show that charcoal must be heated at approximately 1000° or above to produce negative adsorption from solutions of sodium hydroxide.
4. Quantitative data have been presented illustrating the practical impossibility of removing even a feebly adsorbed acid such as hydrochloric from charcoal by repeated extraction with boiling water.
5. Adsorbed hydrochloric acid can be quantitatively removed from charcoal by electrodialysis.
6. No one theory alone seems capable of explaining satisfactorily all the known facts of adsorption of electrolytes by adsorbent charcoal.

East Lansing, Michigan.

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- 20 Miller: J. Phys. Chem., 31, 1197 (1927).
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THE REMOVAL OF SULPHUR COMPOUNDS FROM PETROLEUM DISTILLATES

BY HARRY N. HOLMES, A. L. ELDER, AND NORVIL BEEMAN

Sulphur removal has always been recognized as a problem of great importance in the petroleum industry though it may not be as serious as at one time thought. Consultation of the literature will reveal a wide range of materials which have been used either as chemical reagents or as adsorbents to bring the sulphur content of petroleum distillates within the 0.10% limit of the federal government's specifications. The chief chemical reagents for sulphur removal are: sulphuric acid, chlorine and the hypochlorites, liquid sulphur dioxide, and lead plumbite. The principal adsorbents include: fuller's earth, charcoals and activated carbons, clay, bauxite, alumina, and silica gel. On the whole the adsorbents are also excellent clarifiers and it is probably in this rôle that they find, in general, their greatest usefulness.

Silica Gels

Of all the adsorbents, silica gels properly treated, seem to be the most effective both as desulphurizers and as clarifiers. Their advantages lie in the fact that they do not remove such a high percentage of unsaturates or "anti-knock" material as does sulphuric acid.

On page 366 of the Handbook of Petroleum¹ there is shown the following graph, Fig. 1, to illustrate the effect of sulphuric acid treatment upon a distillate containing about 0.87% sulphur. One curve shows the effect of different concentrations of sulphuric acid in pounds per barrel in lowering the sulphur content, while the other shows the loss in volume (largely unsaturates) which accompanies this treatment. Thus with 20 lbs. per bbl., for example, the sulphur was reduced from 0.87% to 0.33%, but this treatment caused a volume shrinkage of 8% to 9%; with 30 lbs. per bbl., the sulphur was reduced to 0.25% but with a 14% loss; with 40 lbs. per bbl., sulphur was reduced to 0.19% with a 20% loss. Heavy sulphuric acid treatment causes not only volume loss but lowers the anti-knock quality as well.

The same handbook gives on page 367 an estimate of the loss of anti-knock materials which accompanies the loss of unsaturates:

8 lbs. H_2SO_4	decreases the anti-knock value	4.2%
20 lbs.	" " " " "	10.6%
30 lbs.	" " " " "	21.2%
40 lbs.	" " " " "	25.5%

¹ Handbook of Petroleum, Asphalt and Natural Gas. Bulletin No. 25, Kansas City Testing Laboratory.

Experimental work with silica gel as a desulphurizer has been reported upon by Youtz and Perkins,¹ Borgstrom, Bost and McIntire,² Waterman³ (who in two treatments with 54% silica gel decreased the sulphur content of a Persian oil 20%), Challenger⁴ (who calls attention to the fact that silica gel removes only some sulphur compounds from mineral oils), Holleman,⁵ Koetschau⁶ (with a review of the literature), Miller^{7,8} (with description of an oil refining plant using powdered silica gel), Waterman and Perquin,⁹ Waterman and Tussenbroek,¹⁰ Wood^{11,12} (who studied the removal of sulphur and sulphur

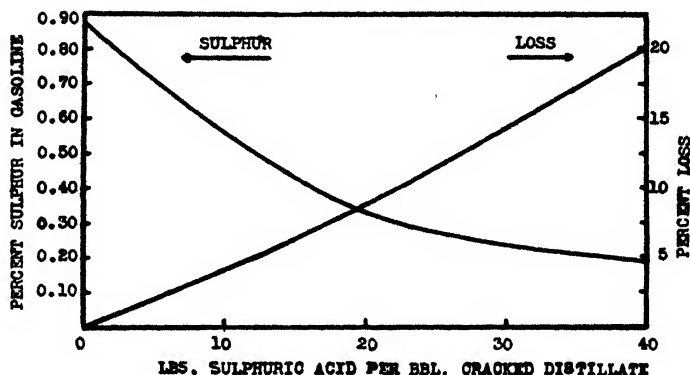


FIG. 1

compounds from naphtha and found silica gel better than fuller's earth and alumina), Gladys E. Woodward¹³ (who found that from a naphtha solution a commercial gel removed 18% and a Holmes' gel 37% of the sulphur), and Bosshard and Wildi¹⁴ (who suggest that in treating lubricating oils the coloring matter may be removed by a preliminary treatment with gels having coarse pores followed by gels with finer pores for sulphur removal).

The Sulphide-Coated Gels

Although ordinary silica gel, activated but otherwise untreated, is a good remover of sulphur compounds from petroleum oils, the senior author early planned to use silica gel coated with metallic sulphides.

¹ Ind. Eng. Chem., 19, 1247 (1927).

² Ind. Eng. Chem., 22, 87 (1930).

³ J. Inst. Petr. Tech., 11, 576 (1925).

⁴ Ind. Chem., 2, 445 (1926).

⁵ Chem. Weekblad, 21, 187 (1924).

⁶ Chem.-Ztg., 48, 497 and 518 (1924).

⁷ Oil and Gas J., 23, 104, 151, 158 (1924).

⁸ Trans. Am. Inst. Chem. Eng., 15, 241 (1923).

⁹ Brennstoff Chem., 6, 255 (1925).

¹⁰ Brennstoff Chem., 9, 397 (1928).

¹¹ Oil and Gas J., p. 146, Feb. 24, 1927.

¹² Ind. Eng. Chem., 18, 169 (1926).

¹³ Ind. Eng. Chem., 21, 693 (1929).

¹⁴ Helv. Chim. Acta, 13, 572 (1930).

It might be thought that PbS, CuS, etc., freshly prepared and activated could serve alone without the support of a gel structure. This was tried in the Johns Hopkins Laboratory¹ and it was found that "ethyl mercaptan was readily removed when shaken with amorphous cupric, lead, stannic, cadmium and arsenious sulphides. Cupric sulphide was immediately affective as an adsorbent for the removal of secondary amyl mercaptan." It would have been more interesting if this work had been done on an actual petroleum distillate from which the sulphur compounds are almost always less readily removed than a comparatively simple mercaptan. One of us (A.L.E.) working with a cracked California distillate was able to get only a negligible sulphur removal with precipitated and activated CuS. The conclusion reached was that CuS without the support of the gel did not offer a sufficiently large area of active surface for the appreciable removal of sulphur compounds commonly found in cracked petroleum distillates.

The Silica Gel Support

The gel used as a support for the sulphide coating was that known colloquially in this laboratory as "white gel" or "gel from iron." Instead of precipitating the silicic acid gel from water glass by the addition of HCl,* gel is prepared by stirring together intimately dilute solutions of FeCl₃ and sodium silicate in such proportions as to give a mixture neutral to litmus.^{2,3} Time is given for the gel to set and drain. It is then broken into lumps and allowed to dry to about 45% water content when it is bottled to synerize for a few days. The "red gel" resulting, actually a molecular mixture of the hydrated oxides of iron and silicon, may itself be activated and used as an adsorbent.

However, the support we employed for sulphides was not the "red gel" but the "white gel." To obtain the "white gel" from the chocolate-brown material, the "wet-heat treatment" is given with hot 0N H₂SO₄. This removes the ferric oxide leaving when dried at 150° to 200° a white porous product of slightly hydrated silica.

This particular "wet-heat treatment" produces a gel of the "medium vitreous" type and which was found by Ross⁴ to be, when coated with CuS, the most efficient sulphur remover of all the similarly coated gels with which he worked. In contrast to this it might be pointed out that Holmes and Elder⁵ found that the benzene-adsorption capacity of the Holmes' "chalky gel" was far greater than the vitreous and glassy type. As has been pointed out, the "wet-heat treatment" provides an excellent means of securing any desired capillary size from the "vitreous" which has the appearance of broken china with capillaries averaging 8 to 10 mμ in diameter, to the "chalky," which possess a soft, easily powdered structure with capillaries from 10 to 20 mμ. The

* U. S. Pat. 1,297,724 by Silica Gel Corporation.

¹ Ind. Eng. Chem., 21, 1033 (1929).

² Ind. Eng. Chem., 17, 280 (1925).

³ Ind. Eng. Chem., 18, 386 (1926).

⁴ Master's Thesis, Oberlin College, May (1931).

⁵ J. Phys. Chem., 35, 82 (1931).

commercial gel of the Silica Gel Corporation is of the hard, glassy type with capillaries approximately 4 to 5 μ in diameter.

In general the higher the water content before the "wet-heat treatment" and the higher the temperature of the water or the acid of the "wet-heat treatment," the larger the capillaries.

The Sulphide Coating

Various methods of securing uniform deposits of finely divided metals, metallic oxides and sulphides throughout porous solids have been investigated in this laboratory.¹ The best CuS coating is secured by soaking the "white gel," obtained by a 45%–60° "wet-heat treatment," in a solution of CuSO₄, draining off the excess CuSO₄, drying for about two hours in nitrogen or CO₂, cooling to 0° and saturating with H₂S gas, washing and drying up to 200° in an inert gas such as nitrogen or CO₂. Free sulphur is always formed in the gel in this process and it must be removed before the gel can be used as a desulphurizer.

The possible source of the sulphur found in the CuS coated gel at this stage in its preparation may be H₂S or CuS both. The H₂S may be cracked on the gel surface, or it may be so strongly adsorbed by the CuS coating that even repeated washing does not remove it. In the latter event, it is left to be cracked later when the gel is heated for activation.

That it is possible for H₂S to be strongly adsorbed by CuS was pointed out in 1892 by Linder and Picton² and more recently by Kolthoff.³ There is little reason to suppose that CuS should hold H₂S more strongly than other sulphides, PbS and CdS, for example. As a matter of fact PbS coated gel and CdS coated gel may both be washed until free from sulphide ions. When heated in nitrogen neither washed product gave the slightest evidence of free sulphur. We are forced to turn then to the other possible source, the CuS itself.

It is well known that CuS breaks down at red heat in the absence of air into Cu₂S and free S, and that the Cu₂S is stable over a wide range of temperature. This decomposition probably occurs to a limited extent at lower temperatures. When the gels were heated in exactly the same manner the CuS gave a sulphur deposit upon the tube walls while the PbS and CdS coated gels did not.

Activation and Use of Adsorbents

When the CuS coated gel is heated any free sulphur formed is driven off and activation is accomplished by the same process and at the same time. As might be expected the time period and the temperature at which the activation is carried out has a profound influence upon the efficiency of the gel as an agent for removing sulphur compounds from petroleum oils.

In the investigation of activation temperatures a series of experiments was run with different types of gels, 10–20 mesh, on an untreated California

¹ Colloid Symposium Monograph, 6, 283 (1928).

² J. Chem. Soc., 61, 120 (1892).

³ J. Phys. Chem., 36, 861 (1932).

cracked distillate* containing 0.363% sulphur. The procedure with each gel was to shake 3 volumes of the gel with 5 volumes of the distillate for $1/2$ hour, decant off the oil, centrifuge it, filter, and analyze by the sulphur lamp. The main purpose of these experiments was to determine the activation temperature with each gel which gave the maximum sulphur removal. It would probably be unwise to draw conclusions from this series as to the relative superiority of one type of gel over another, because the original gels from which these were prepared differed one from the other in water content and other respects. It

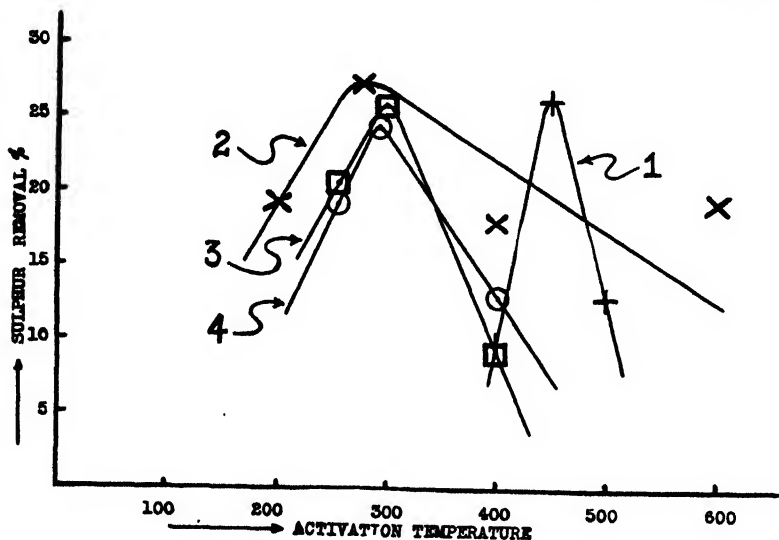


FIG. 2

Effect of Activation Temperature upon Sulphur Removal.

Curve 1: CuS coated gel, activated in nitrogen.

Curve 2: "Red gel" activated in air.

Curve 3: "Red gel" kerosene treated, activated in nitrogen.

Curve 4: "Red gel" kerosene treated, activated in air.

would have been interesting, for the sake of comparison, had the gels all come from a common source, but this was not so and the reader must be warned against drawing unwarranted conclusions.

Curve 1 of Fig. 2 is that of a CuS coated "white gel" which had been given a "wet-heat treatment" of 42.2%–60°. The gel was activated two hours with slowly rising temperature in an electric tube furnace in a stream of nitrogen. For each activation the gel was placed in the furnace at room temperature, the air swept out by nitrogen, and the electric current turned on. The temperature was measured with a thermocouple. It is observed that the maximum on the curve falls on the 42.2° ordinate with a removal of 26.6% sulphur. To the left of the maximum the curve in reality drops below the horizontal axis (not shown in the figure) because at these lower temperatures the sulphur formed by the decomposition of the sulphide is not all driven off, with the consequence that

* The California distillates used in this work were furnished through the courtesy of the Universal Oil Products Company, Chicago, Illinois.

the distillate actually dissolves the sulphur during treatment, and, instead of removal, there is an actual increase in sulphur content of the oil. To the right of the maximum the curve again falls off rapidly but never to a zero removal. This drop to the right may be explained in part by the change of the CuS to Cu_2S . Each point through which the curves are drawn is an average of two or more determinations and in some instances a half dozen or more. The general shape of the curve was confirmed by subsequent work and there can be little question about the location of the maximum.

A study of this curve and a consideration of the facts brought out in connection with the discussion of the presence of free sulphur in the gel, suggested that a vacuum activation at lower temperatures would prevent to some extent the decomposition of the CuS and at the same time make removal of the sulphur possible at lower pressures and lower temperatures. This was done and the best and most consistently high removals of sulphur from gasoline were obtained by CuS -coated gels activated in this manner. The gels were heated in nitrogen at a pressure of 2.0–2.5 cm at temperatures ranging from less than 200° to about 300°C . Over the range between 225° and 270° the best results were obtained. Gels treated in this manner removed more than 30% of the sulphur.

The other curves in Fig. 2 have to do with the same distillate but treated with different "red gels," though the proportions, time of treatment, etc., were in general the same as with the CuS -coated gel. Curve 2 is that of a "red gel" activated in air. With this gel the maximum sulphur removal occurs with an activation temperature of about 275°C at which 27.6% of the sulphur was removed from the distillate.

Curve 3 is for another "red gel" but with the difference that it was dried below 200° before activation, soaked in kerosene for a day, drained, and then activated in a slow current of nitrogen. Here the maximum is the average removal of 26.2% and falls on the 300° ordinate. Similarly Curve 4 is for a "red gel" kerosene-treated but activated in a current of air. The maximum represents a removal of 24.8% when the gel was activated at 290°C .

Duplication of these curves is not difficult when the preparation of the gels is carefully controlled, that is, when the water content of the original gels is always the same before "wet-heat treatment," and the activation carried out each time in exactly the same way.

The Sulphur Lamp

The sulphur analyses were made with the A.S.T.M. lamp. From time to time in recent years several changes have been proposed in this lamp for the purpose of increasing the accuracy and of making it more generally useful in the analysis of various grades of oil. Some of these more recent suggestions have come from: Wood and Mattox¹ with a cooling device for regulating the flow of oil, thus rendering it more satisfactory for both heavy and light oils; Edgar and Calingaert² with a metal collar to radiate the heat away from the

¹ Ind. Eng. Chem. Anal. Ed., 2, 24 (1930).

² Ind. Eng. Chem. Anal. Ed., 2, 104 (1930).

flame and a porous fritted glass disc in place of the beads in the adsorption tube; from Luis Bermejio Vida¹ making use of a long quartz combustion tube in which the sample is placed after being soaked up in absorbent cotton and said to give results equal to or a little higher than the bomb; and Formanek² with an improvement on the apparatus of Engler-Heusler permitting a larger flame, faster burning of the oil, and better absorption of the sulphur oxides.

The form used in this laboratory during 1931-32 is shown in Fig. 3. The essential difference from other forms lies in the sliding glass collar which makes possible a quick adjustment of the flame. This glass collar is held in place by the radiator of sheet brass which in turn is held by two spring clamps to the wick tube of the lamp. At first, our method of analyzing heavy oils was the somewhat doubtful one of diluting with a good grade of gasoline before placing it in the lamp, but later the lamps were fitted with a small "pilot flame" which burned sulphur-free alcohol. A small test tube holding the alcohol, stoppered with a slotted cork carrying a long wick tube was clamped in such a way as to bring a small alcohol flame to the wick of the sulphur lamp. This auxiliary flame served to steady the burning by warming the heavy oil just at the proper place and by reducing appreciably the formation of tarry crusts over the end of the wick.

Some idea of the accuracy obtained by the lamp may be given by saying that in ordinary routine analyses of gasolines the variation of any one determination from the average of a triplicate run did not exceed 4% of the total sulphur except when unusual difficulties were experienced, such as excessive gumming or encrusting of the wick. The amount of oil burned for each determination was approximately one gram, determined by taking the difference in weight of the lamp before and after burning.

It was thought that some of the inaccuracy of the lamp might be due to the fact that not all sulphur was burned to SO_3 . If burned only to SO_2 instead of SO_3 , more acid would be required in titration and this would give an apparently lower sulphur content in analysis. In order to get some evidence at this point an investigation was made of the amount of SO_2 converted into SO_3 during the burning in the lamp of a solution of SO_2 in a sulphur-free alcohol. The SO_2 was

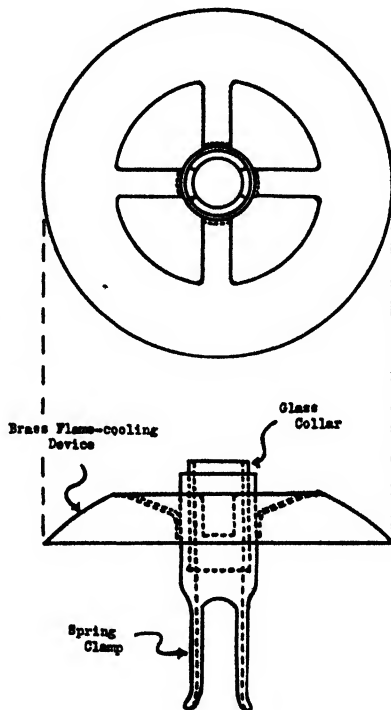


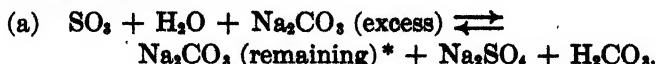
FIG. 3
Sections of Flame-cooling Device for the Sulphur Lamp

¹ *Chimie et Industrie*, Special No., 189-95, March, 1930.

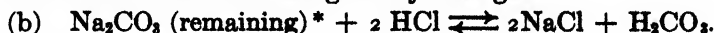
² *Chem. Absor.*, 6, 36 (1931).

taken from a small lecture table cylinder of the gas. After the burning the sulphites which were formed by reaction between the SO_2 and Na_2CO_3 were determined by iodine titration. If only SO_2 and no SO_3 had passed over into the Na_2CO_3 we would have:

In the absorption tube:

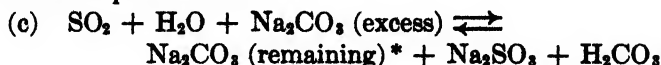


In the titration with acid using methyl orange:



If only SO_2 and no SO_3 we would have, on the other hand:

In the adsorption tube:



In the titration:

(d) same as (b)

(e) $\text{Na}_2\text{SO}_3 + \text{HCl} \rightleftharpoons \text{NaCl} + \text{NaHSO}_3$ and then a slight excess of acid would give the end point with the indicator.

Now it was found by analysis of the solution in the absorption tube that about 90% of the SO_2 had been converted into SO_3 leaving 10% unchanged. An examination of the equations involved makes it plain that except for equation (e) the amount of acid required in a titration would be the same whether the gas were SO_2 or SO_3 . But if 10% is SO_3 , since in accordance with equation (e) the sodium sulphite would act with methyl orange as a mono-acid base, 5% more acid would be required to give the end point and the analyst would report 95% of the sulphur present.

It is interesting to note that Wood and Mattox with their modified lamp accounted for 92% to 95% of the sulphur (as carbon disulphide) present in gasoline and kerosene, and that Edgar and Calingaert accounted for 95.7% in pure heptane.

Results with Sulphide-Coated Gels

1. *Sulphur from Gasoline.* One of us (A.L.E.) working with a gasoline which contained 0.597% sulphur, treated it with several different sulphide-coated "chalky" gels and obtained the results tabulated below. Three volumes of the gel were shaken for 1 hour at room temperature with 5 volumes of gasoline:

Gel coating	% S after treatment	% S removal
MnS	0.430	12
PbS	0.479	20
FeS	0.447	25
Ag ₂ S	0.430	28
CuS	0.405	32

* For the sake of simplicity this is left as Na_2CO_3 , but of course it would be largely the bicarbonate formed in the presence of CO_2 during the combustion of the oil.

It is seen from this that CuS-coated gel is more effective as a sulphur remover than any of the others mentioned.

2. *Thiophene from Gasoline.* From a solution of 0.597% thiophene by weight in a very good quality of gasoline 34% was removed by treatment with CuS-coated chalky silica gel at a temperature of -10°C , while PbS-coated gel removed only 24%. When the temperature was lowered still more by cooling with CO_2 snow the removal with CuS gel was 42% and with PbS 32%.

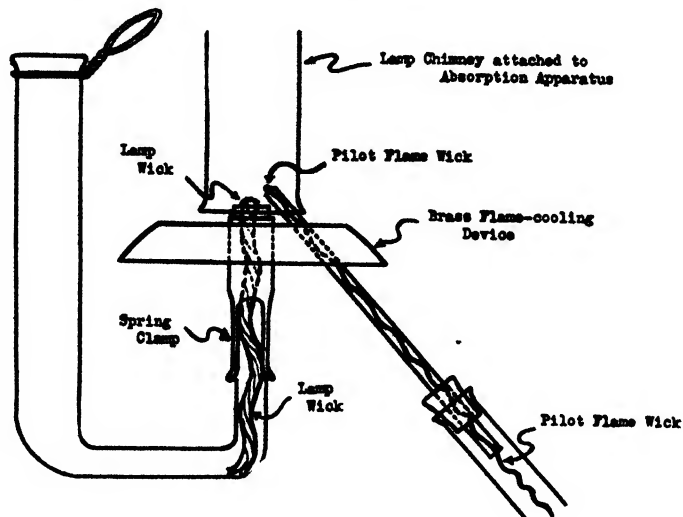


FIG. 4

Sulphur Lamp Assembly for Heavy Oils

(A.L.E.) This increased removal at the lower temperature strongly indicates adsorption as a part of the removal action.

It is rather to be expected that removals are generally a combination of adsorption and chemical reaction. For some compounds adsorption predominates.

3. *Sulphur from Shale Oil.* Thick viscous oils have a tendency to cover the outside of the gel particles and thus block the capillaries and prevent free access of the oil to a large part of the active surface of the gel. To meet this problem our shale oil was fractionated and the fractions worked with separately. The lighter the fraction the more easily was the sulphur removed, but even with these lighter fractions gumming of the gel was a source of trouble and the sulphur removals small.

A fraction boiling between 250°C and 300°C was treated for one hour by shaking with CuS-coated gel in the ratio of 3:5, by volume of gel to oil, and the sulphur content was reduced 9.8%. On the other hand, a fraction boiling between 300°C and 350°C showed no removal with the same treatment. But this same fraction after a preliminary treatment with 6 grams anhydrous AlCl_3 per 100 cc. oil gave a total removal of 10.3% when followed by treatment with CuS-coated gel.

An entirely different fraction, boiling between 200°C and 250°C, was treated as follows:

Preliminary treatment		Followed by	
Reagent	% removal	Reagent	Total % removal by both
CuS gel	nil	—	—
AlCl ₃	nil	CuS gel	9.9%
H ₂ SO ₄	1.9%	CuS gel	13.8%
"Red Gel"	0.7%	CuS gel	16.5%

In reviewing all the work with shale oil it can be said that preliminary treatments in general averaged less than 5% removal. These preliminary treatments, however, evidently removed substances which interfered with the effectiveness of the CuS-coated gel, for when followed by a treatment with the gel better removals were obtained than with the gel alone. The above table is presented to show the general tendency discovered, not to claim decimal point accuracy for the results obtained.

Freshly fractionated shale oil was generally light in color but darkened rapidly with age. After a time a gummy sludge invariably settled out.

4. *Use of Regenerated CuS-coated Gels with Gasoline.* A CuS-coated gel, 10–20 mesh, which had previously removed about 25% sulphur from an untreated distillate, was recovered by heating in nitrogen gas at a temperature of 275°C. It was then again used in the treatment of a fresh sample of the same distillate and found to remove 25.4% sulphur. Another CuS-coated gel, powdered to 50 mesh, was recovered in the same manner and found to take 29.9% sulphur from a fresh sample of the distillate.

Regeneration by roasting in the air was also tried, since this, if feasible, would be somewhat cheaper on an industrial scale than regeneration in nitrogen or carbon dioxide. But the roasting would have to be so carried out that the CuS did not oxidize excessively. It was very interesting to discover that the heating of a 10 to 15 gram sample of once-run CuS-coated gel in an open dish until it catches fire and burns off without further external heating makes just about the right combination of length of time and height of temperature. The temperature rises in such a roasting to 380°C or 400°C but that temperature is maintained only for a few minutes. Larger samples would probably heat up more, especially if stirred during the burning off. Some of the once-run CuS-coated gel, 10–20 mesh, mentioned above, was thus heated in an open dish and as soon as the flame had died out and the gel cooled somewhat, was used in the treatment of a fresh sample of distillate with the result that 28.2% of the sulphur was removed. It was similarly reactivated again and upon the third treatment of a fresh sample there was an average removal of 27.3%.

These re-runs with re-generated gels are significant in that they point to the recovery and re-use of the gels a number of times before they become exhausted. Even after use and recovery two times, when the re-generation was by a method calculated to be very severe upon the gel, little deterioration was shown, for on the third run almost as much sulphur was removed as before.

Results with a Silica Gel

The uncoated silica gel, *i.e.*, the "white gel," was found to have a powerful adsorbing action for sulphur compounds in gasoline but on the whole was not as good a sulphur remover as the CuS-coated gel. The vitreous type of silica gel removed sulphur better than the very chalky, but a semi-chalky gel was the best of all.

A "white gel" which had been given a preliminary treatment with kerosene after activation was the most satisfactory of the "white gels" for sulphur removal. (A.L.E.) Thus a gel of the vitreous type was shaken with a distillate containing 0.76% sulphur. The ratio of gel to oil was 3:5 by volume and the period of treatment one hour. The removal obtained was 32%. But when this gel was given a preliminary kerosene treatment the removal was increased to 40%, one of the highest single removals with kerosene-treated silica gel. A sample of Patrick's gel under similar conditions removed 36% and after it had been given the kerosene treatment removed 37%. (A.L.E.) In another treatment of the same distillate with the same ratio of gel to oil, using the Holmes' semi-chalky gel, kerosene treated, the removal was 30%. The more vitreous Patrick's gel, used in the same way including kerosene treatment, removed 20%. It is evident that the semi-chalky gel with the larger pores removes sulphur from gasolines more efficiently. (A.L.E.)

Results with the Red, Hydrated Ferric-Oxide-Silicon-Dioxide Gel

A vitreous type of "red gel" prepared from sodium silicate and ferric chloride in such proportions as to be neutral to litmus, was the type of this gel most favored for sulphur removal. (A.L.E.)

A California distillate containing 0.76% sulphur treated for 1 hour at room temperature with this neutral type of "red gel," in the ratio of 3:7 gave a removal of 14%, while another in the ratio of 3:5 removed 23%. This latter, after a preliminary treatment with kerosene, was much improved and removed 27%. Other "red gels," after receiving the kerosene treatment, removed sulphur from gasoline as follows: one in the ratio of 1:2 after a 4 hour shaking with the sample removed 24%, another in a 2:3 ratio and a 3 hour shaking removed 27%. In all these preliminary treatments of the gel, kerosene proved better than gasoline or any light oil. (A.L.E.)

It was noted that lower fractions of refined and redistilled kerosene did not do as well as the higher in the matter of sulphur removal. This lends support to the idea that oil used for this preliminary treatment must be of sufficiently high boiling point to drive off water adhering to the gel surface. Dunstan, Thole and Remfry¹ have pointed out in connection with their experiments with bauxite that if air is admitted to the freshly activated bauxite it becomes less active. This same thing may be said here in connection with the gels. The oil may not only drive off water but may prevent or delay adsorption of moist air on the gel surface.

Double Treatments; Combination Treatments

By double treatment is meant the further treatment of the same, already treated distillate by a fresh sample of gel. Double treatments of shale oil have been reported upon in the paragraph on "Sulphur from Shale Oil." Double treatments of gasolines follow here.

One of the best results from double treatment was obtained with a vitreous "white gel" of 20 mesh on a California distillate containing 0.76% sulphur when 50 cc. of the gel were shaken with 100cc. of distillate and then allowed to stand for 12 hours. Upon analysis this treatment was found to remove 24% of the sulphur. A second treatment of this once-treated distillate in exactly the same manner with a fresh sample of gel gave a further removal of 21%, or a total by the combined treatments of 55%. This was repeated and the average of the two sets of double treatments came to 47%. (A.L.E.)

Color Removal

The "red," "white," and CuS-coated gels all remove color very well. The concentration ratio of 3 volumes of gel to 5 volumes of distillate can always be counted upon to remove about 95% of the color by shaking them together for $\frac{1}{2}$ hour.

The best color removal obtained was with a "white" gel which had received a preliminary treatment with oleic acid. This gel in the ratio of 2:5 removed all the color from a California distillate when shaken for 1 hour. (A.L.E.) "Red gel" is also a very effective color remover, both kerosene treated and untreated as 3 volumes of "red gel" shaken 1 hour with 5 volumes of distillate removed 99% of the color. (A.L.E.)

Regenerated gels, both "red" and CuS-coated, were found to remove almost all the color from brownish yellow gasoline. Samples of these gels regenerated in an open dish by heating until they caught fire, when shaken for $\frac{1}{2}$ hour in the ratio of 3:5, removed 99% of the color.

Effect of Aging upon Cracked Distillates

Though this matter has not been investigated thoroughly, it has been observed that the sulphur compounds in cracked distillates undergo change with age. The insides of containers become covered with a thin dark deposit and the sulphur compounds evidently change in composition or polymerize or become altered in such a way as to show a lower sulphur content upon analysis with the sulphur lamp. Variation in results obtained over a period of months or years through the use of gels prepared in much the same way is explained by this aging of the distillates and change in the sulphur compounds with consequent change in the ease with which the sulphur compounds can be removed.

Summary and Conclusions

1. It has been shown that cupric sulphide is superior to other metallic sulphides in removing sulphur compounds from petroleum distillates.

2. Silica gels, thoroughly impregnated with cupric sulphide, are superior to metallic sulphides without the gel support.
3. The efficiency of the sulphide-coated gels varies greatly with the activation temperature.
4. During activation of the cupric sulphide—silica gel free sulphur is released, in the formation of cuprous sulphide, and must be driven out by adequate heating.
5. The gels described may be regenerated and used repeatedly with good results.
6. Adsorption methods of sulphur removal do not, like the sulphuric acid treatment, cause a heavy loss of valuable anti-knock fuel.
7. An improved form of sulphur lamp for the oil industry is described.

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Oberlin, Ohio.*

THE STUDY OF GELS BY PHYSICAL METHODS

BY EMIL HATSCHEK

The present paper is in the main a record of experimental investigations which do not claim to be more than the first steps in two distinct lines of inquiry. It seemed to me first of all desirable to gain some insight into the elastic properties of a number of gels other than gelatin, which so far has almost exclusively received the attention of investigators and, with the exception of the benzyl alcohol gel of cellulose acetate, is the only one for which Young's modulus has been determined for a range of concentrations. A knowledge of this constant appears to be indispensable for forming any idea of the structure of a given gel, and I have accordingly determined by a method not hitherto employed the modulus of agar gel, silicic acid gel and formaldehyde-gelatin gel, as well as followed its variation with age.

In the second place it seemed advisable to study the effect of deformation on various physical properties of one gel more exhaustively than has been done so far, and to discriminate between the changes brought about by reversible and irreversible deformation. Gelatin is most convenient for this purpose. The investigation, so far as it has been carried, covers the changes produced by both types of deformation in (a) accidental birefringence, (b) tensile strength and (c) permeability to a solute, *i.e.*, diffusion velocity in the gel.

Finally some of the theoretical implications of the experimental findings are discussed very briefly.

The first physical constant of gelatin gels to be measured was Young's modulus. The earlier investigations by Maurer, Bjerken, Fraas and Leick¹ may be assumed to be generally known. They were undertaken with a view to studying the elastic behaviour of a material in which small stresses produced considerable deformations and optical anisotropy which could be readily observed, while it exhibited in addition interesting anomalies; a combination of features which have no doubt secured for the results inclusion in the hand-books of physics, like Winkelmann's. The intensive study which gelatin sols and gels have received within the past two decades has produced further determinations of Young's modulus, carried out with somewhat different intentions, such as testing the validity of mathematical deductions from assumed structures, among which must be specially mentioned those by Sheppard and his collaborators² and by Poole.³

It is a striking illustration of the strength of tradition or of habit that, with the exception of Sheppard's, all measurements have been made on test pieces in tension. This is the obvious method for *e.g.*, metals, but in adapting

¹ Maurer: Wied. Ann., 28, 628 (1886); Bjerken: 43, 917 (1891); Fraas: 53, 1074 (1894); Leick: Drude's Ann., 14, 139 (1904).

² J. Am. Chem. Soc., 43, 539 (1921).

³ Trans. Faraday Soc., 21, 114 (1925).

it to gel specimens the earlier workers found some difficulty in clamping the ends. This difficulty is now avoided by Sheppard's method of attaching the ends of the specimens to wood blocks—a method used successfully by Poole on gels of as low concentration as 3.23%, which could not conceivably have been handled in tension by any other method—the application of which is, however, obviously confined to gels which adhere to wood. The only one of this kind which has so far been investigated, also by Poole,⁴ is the benzyl alcohol gel of cellulose acetate, which in its general elastic behaviour closely resembles gelatin gel.

It is difficult to see why apparently no attempts have so far been made to determine Young's modulus by compression. The method has obvious advantages even for adhesive gels, and is applicable to gels which cannot be attached to supports or clamped, such as agar and silicic acid gels. Although a re-determination of the modulus of gelatin gels is not one of the main objects of the work to be described in the present paper, a good deal of it is concerned with the changes produced in various properties of gelatin gels by compression and the method was therefore first tested on such gels.

The test pieces were cylinders, mostly 31.5 mm in diameter, with plane ends, the length not exceeding 1.4 diameters. If the test piece is to keep—very approximately—cylindrical under pressure, the plane ends must slide freely over the surfaces between which they are compressed. It is difficult—at any rate I have found it so—to cut gelatin cylinders, especially at the lower concentrations examined, so that the resulting surface will be really plane and will slide freely even over oiled metal surfaces. It therefore appeared desirable, and was in any case necessary for the diffusion experiments to be described later on, to produce the two plane end faces directly on the castings. There is of course no difficulty in obtaining one plane end, by using a cylindrical mould closed at one end by a plate of some material to which gelatin does not adhere, but the free surface on cooling sets to a concave meniscus, even if the mould consists of a material to which gelatin does not adhere. The procedure finally adopted for all cylindrical gelatin specimens was as follows: the moulds were lengths of brass tubing cut off in the lathe. One end was closed by a shallow flat metal dish in which sufficient paraffin wax had been melted to form a layer about 2 mm deep. The previously warm lengths of tube were placed in the dishes which stood on a levelled table and were allowed to cool on it. The moulds were carefully greased with vaseline and filled with the gelatin sol at a temperature of 35 to 40°. To avoid meniscus formation sufficient liquid paraffin, a few degrees warmer than the sol, to form a layer 2 or 3 mm deep is poured on the sol and, like the paraffin wax in the bottom, forms a small concave meniscus with the wall. The gel cylinder is accordingly bounded by two plane ends at right angles to the axis and the two circular edges are rounded off by the menisci. While this makes the pressure distribution a little less regular than it would be in the absence of the rounding off, these test pieces slide more freely than any cut faces which I have ever managed to produce. The mould is illustrated in Fig. 1.

⁴ Trans. Faraday Soc., 22, 82 (1926).

The determination of the modulus was carried out in the press illustrated in Fig. 2. The top plate A' was gun metal in one case, and aluminium in others, to reduce the minimum load which could be used. It was further loaded by "cheeseweights," viz. small tins filled with shot and weighing 200 gm each. The press was mounted with the measuring microscope on a common levelled base plate. The faces A A' were well oiled or vaselined.

The specimens were loaded, first with the top plate alone, and then with successive further loads of 200 gm each and the lengths, either between the ends of the specimens, or between Indian ink marks placed near the ends, read

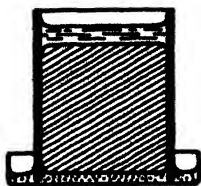


FIG. 1

by the microscope. No intervals were allowed for recovery between the readings, which thus occupied a few minutes only. The specimens were always allowed to age for at least 24 hours before being removed and were then assumed to be at the temperature of the room. The own weight of the specimen was not taken into consideration, but E was calculated from

the true stresses, which were calculated from the known loads per cm^2 of original cross-section on the assumption that the volume remained constant, so that the cross-section increased in the same ratio as the length was reduced.

Although the result was hardly in doubt it seemed to me desirable to ascertain on at least one specimen how the values of the modulus found by compression compared with those obtained in tension. A cylindrical specimen 25 mm dia. and 72 mm long was accordingly prepared in accordance with Shepard's method and a central portion 49.8 mm long (which remained very approximately cylindrical during extension) marked off for observation. The results, as well as those obtained in compression on a specimen 31.5 mm dia., cast at the same time and otherwise treated exactly alike, are given in Table I.

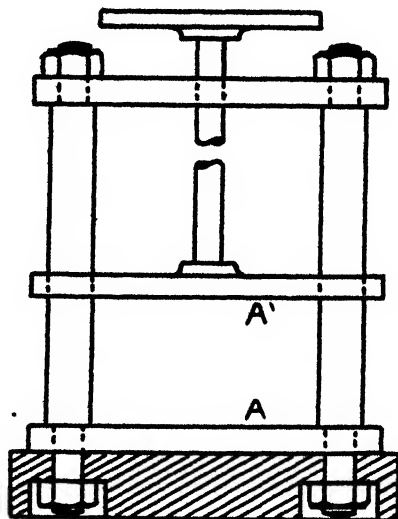


FIG. 2

The modulus apparently increases with increasing elongation and decreases with increasing compression. Whether the increase with tension is that observed by Poole (l. c.) and postulated on theoretical grounds (to which the decrease with increasing compression would seem to be a necessary corollary) or is the cumulative effect of the small irreversible deformation, need not be

TABLE I

Young's Modulus of Gelatin Gel (10 gm gelatin in 100 gm water) by Tension and Compression

(In this and all subsequent tables loads are given in gm, lengths in cm, and stresses and E in gm/cm²).

A. By Tension. (Temp. 17.0°)				
Load	Length	Percent of original length	Stress	E
0	4.98	100	0	—
17.3	5.05	101.4	3.58	255
123.3	5.48	110.0	27.61	276
173.3	5.67	113.8	40.17	291

B. By Compression. (Temp. 17.0°)				
Load	Length	Percent of original length	Stress	E
0	2.70	100	0	—
157	2.50	92.6	18.7	250
357	2.27	84.0	38.5	239
557	2.06	76.3	54.8	231
757	1.90	70.3	68.9	230

discussed, as the exact determination of moduli is not one of the primary objects of this paper. I have, however, thought it of interest to compare a more extensive range of determinations with the values found in the literature and have therefore determined the moduli of four gels, respectively, containing 8, 10, 12.5 and 15 gm of gelatin (dried at 96° and kept in the vacuum desiccator until weighing) to 100 gm of water. The figures given below are the means of the values found at four loads:

Gelatin per 100 gm of water	8gm	10	12.5	15
E in g/cm ²	283	367	480	665
Temperature 13.0°				

The values are somewhat higher than those found by Leick (l.c.) and by Sheppard and Sweet (l.c.), who both worked with hard gelatins. The brand I used appears to be exceptionally hard, and has an ash content—0.6% of the dry weight—remarkably low for a commercial article.

Since the examination of gels other than gelatin by compression offers no difficulty, it appeared desirable to investigate two gels the mechanical properties of which, as far as I am aware, have not so far received any attention at all: agar gel and silicic acid gel.

A 5% agar gel was prepared according to the procedure described by Hatschek and Humphrey.⁵ The (air-dry) agar was soaked in 20 times its weight of water, dispersed at 100° and then kept at about 90° for five or six hours. A greyish coagulum is formed, from which a portion of the clear sol can be decanted, while the rest can be filtered through a plug of glass wool. As agar gel can be cut quite satisfactorily, cylinders were simply cast in a brass

⁵ Trans. Faraday Soc., 20, Pt. 1 (1924).

tube corked at one end; after setting and cooling the cylinders of gel were pushed through so as to protrude a few mm and the meniscus cut off.

As the modulus of 5% agar gel turned out to be surprisingly high, only the higher loads were used. Two determinations are given below. No high degree of accuracy has been aimed at, the object of this investigation being rather to determine the order of magnitude of the modulus of gels not hitherto examined, as a factor to be taken into account in any theories of their structure.

TABLE II

Modulus of Agar Gel (5 gm in 100 gm water) Cylinder 3.5 cm dia.

A. Measured immediately after setting, *i.e.*, about 2 hours after casting

Load	Length	Percent of original length	Stress	E
0	3.598	100	0	—
321	3.560	98.94	33.0	3112
721	3.494	97.11	73.3	2535
921	3.458	96.11	92.0	2365

B. Duplicate specimen, cast at the same time as A and measured 24 hours afterwards

0	3.402	100	0	—
321	3.364	98.88	33.0	2946
521	3.338	98.12	53.1	2826
721	3.304	97.12	72.8	2527
921	3.270	96.12	92.0	2371

The two sets of determinations agree within the limits of experimental error and thus establish an interesting difference between agar and gelatin gels, the modulus of the former not increasing with time, while it is well known that the modulus of the latter does not attain its full value until the lapse of a period for which different values are given in the literature, the rate of increase probably depending on temperature to a greater extent than has been realized.

It is unnecessary to discuss at the moment whether the decrease in the modulus with increasing stress shown in both the series of measurements can be interpreted as evidence of fibrillar structure or is at least in part a consequence of permanent deformation, in which connection it should be mentioned that the specimens on removal of the maximum stress recover immediately to within about 98% of their original length. It is well known that water can be readily expressed out of agar gels, but with the stresses used and during the short time occupied by the whole series of readings no trace of exudation could be observed. If the specimen is left under the maximum stress (92 gm/cm²), a slight dew is visible after 20 to 30 minutes. The 5% gel will support a stress of 350 gm/cm² without fracture and then loses water rapidly; quantitative data, which are of interest in another connection, will be given in a later portion of this paper.

Another gel, the elastic properties of which have received little attention, is silicic acid gel, though Prasad⁶ has determined the modulus of a silicic acid gel (from which increasing quantities of water had been expressed mechanically) by bending a rod of it. For my purpose it was necessary to prepare perfect cylindrical specimens, a task of some delicacy. The two following procedures proved practicable: (a) the type of mould shown in Fig. 1 was employed, but the brass tube was replaced by a tube of filter paper impregnated with paraffin wax. The reaction mixture of sodium silicate and hydrochloric acid was poured in and covered with a thin layer of oil, a sample being set aside to allow observation of the setting and syneresis. When the gel had become firm the whole mould was placed in benzene which dissolved the paraffin in the paper, so that the gel cylinder could, with some care, be removed without injury. (b) An ebonite tube, vaselined inside and having turned edges, was clamped to a thick glass plate, also coated with vaseline, a little rubber grease being applied to the joint from outside to ensure its being perfect. The mould was filled as explained and the whole left until the control showed syneresis, when the glass plate was slipped off in its own plane, and the gel cylinder dropped out of the mould.

The mixture used throughout was: 35 cc of sodium silicate solution of sp. gr. 1.15 into 30 cc of 6 *N* hydrochloric acid (SiO_2 content of the silicate solution 102.9 gm per L.) The mixture set to a gel—*i.e.*, the vessel could be inverted without the surface of the gel showing any sagging—within 3 hours, and perceptible syneresis appeared after 5 or 6 hours.

By using method (b) I managed once to obtain a very perfect specimen which could be removed from the mould intact and submitted to investigation 6.5 hours after casting. The whole series is given in Table III to show the degree of accuracy attainable:

TABLE III
Young's Modulus of Silicic Acid Gel 6.5 Hours Old

Load	Length	Percent of original length	Stress	E
0	4.110	100	0	—
321	3.948	96.06	26.41	670
521	3.840	93.43	42.91	653
721	3.758	91.43	58.11	683
921	3.664	89.14	72.37	666
Mean				668

About 10 seconds after the last reading had been taken, the gel was crushed. In a further series of measurements the gel was accordingly allowed to age longer before removal from the mould, *viz.*, 13 hours. This specimen was also very perfect and was used for following the increase of the modulus with age. The details of the measurements offer nothing new, and only the mean values of E are given in Table IV:

⁶ Kolloid-Z., 33, 279 (1923).

TABLE IV

Variation of Young's modulus of silicic acid gel with age

Age of gel in hours from time of casting	13	24	44	85	133
E	1113	1898	2031	2317	2550

The gel by the end of this series of measurements had developed a few cracks, and the investigation was discontinued, although the modulus was apparently still rising. The values are plotted in Fig. 3, in which the isolated point marked

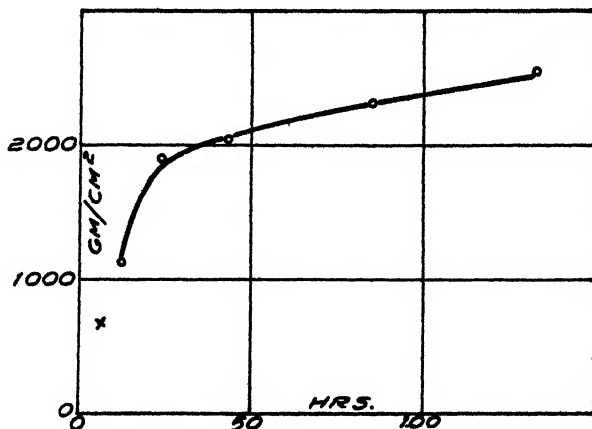


FIG. 3

× shows the value for the gel 6.5 hours old. It falls fairly on the continuation of the curve found for the older gel and is some indication of the reproducibility of the results.

The gel described in Table V continuously lost liquid by syneresis while kept in a saturated atmosphere. The initial and final weights and dimensions only are given below:

Initial		Final	
Weight 51.588 gm	Length 39.78 mm	Weight 43.898	Length 37.46
Diameter 38.00		Diameter 36.00	

On a further specimen of exactly the same composition two sets of determinations only were made; the results were: $E = 806$, 8 hours after casting, and 2520, 83 hours after casting. Considering the uncertainty of the time required for setting the agreement with the values in Table IV is satisfactory.

One further gel, the elastic properties of which had struck me frequently in the course of other investigations, appeared to deserve detailed study, *viz.*, gelatin gel hardened by formaldehyde. Two cylinders were cast in the usual way from sols containing resp. 8 gm and 10 gm of gelatin (dried at 95° and kept in vacuum desiccator) in 100 gm of water. The moduli of both were again determined and found to be 283 and 366, in excellent agreement with the previous determinations. The two cylinders were then placed in a closed

vessel of about 750 cc capacity, lined with several thicknesses of filter paper which was kept moistened with 40% formaldehyde solution. The specimens were weighed and the modulus determined at intervals; as copious syneresis occurs, the diameters were also re-measured at intervals and the loads per unit section recalculated. The results are shown in Table V:

TABLE V
Changes in Gelatin Gels during Hardening by Formaldehyde
8 percent gel

Time in hours	0	48	82	103	165	183	212
E	283	922	2206	2314	2391	2402	—
Weight	30.835	28.973	27.975	27.258	25.714	—	—
Ratio water/gelatin	12.50	11.70	11.26	10.94	10.27	—	—

	10 percent gel						
E	366	1379	2296	2559	4716	4982	5418
Weight	29.905	28.321	27.203	26.691	25.581	—	—
Ratio water/gelatin	10	9.49	8.97	8.76	8.38	—	—

Both specimens developed small cracks at 183 hours, and the investigation was therefore not continued beyond 212 hours. The moduli are plotted against time in hours in Fig. 4, and the curves show several striking features, such as the rapid initial rise of E, followed by an almost abrupt change to a very slow

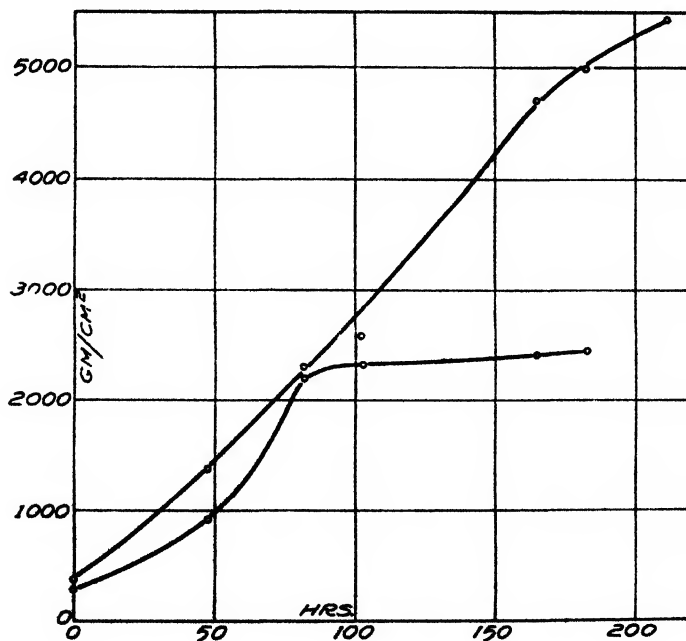


FIG. 4

rate of further increase, and the enormous difference between the 10 and the 8 percent gel as regards the absolute values of E . While there can be no doubt regarding the general course of the hardening process or the order of magnitude of E , the values of the latter are affected by an error due to the change in shape which the specimens undergo. As they lose water they do not retain their cylindrical shape, but, exactly like specimens drying in air, become barrel shaped with convex ends. Although within the range of the present experiments these changes are not too marked, they cannot be altogether allowed for merely by estimating (as has been done) a mean diameter and treating the

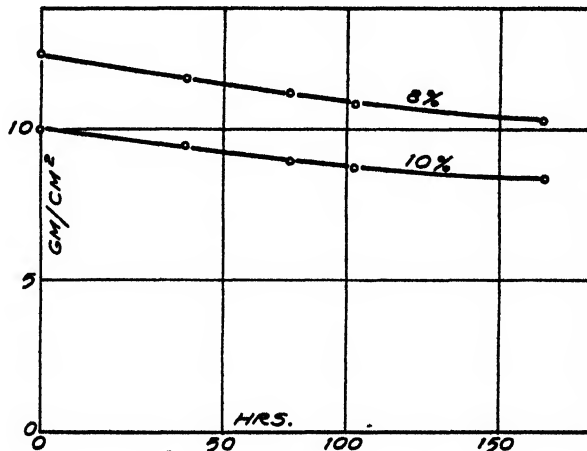


FIG. 5

specimen as cylindrical in the calculation of the stress. The values of the latter, and therefore of E , are likely to be too small, and with exact values the initial convexity of the E - T curves towards the T axis might disappear; the curves would then bear a marked resemblance to the curve for silicic acid gel.

The ratios water: gelatin for both gels are plotted against time in Fig. 5.

The accidental birefringence of deformed gelatin gels has been known for a considerable time, but for the present purpose the only paper in the earlier literature to which reference must be made is one by Reiger.⁷ He determined the relaxation time of gelatin gels by observing the disappearance of double refraction at 29°—a temperature higher than the melting point of most brands of 10% gels, and one at which, according to Poole, the value of the Young's modulus of even a 24% gel falls to less than one tenth of the value at 11.5°. I showed, however, in 1920,⁸ that mechanical relaxation may, at ordinary temperature, have become almost complete, while the optical anisotropy remains practically unchanged. This can hardly be explained on any assumption other than that of a change in structure during the transition from reversible to irreversible deformation, and this assumption has, indeed, been made by later authors who quoted this result. Poole writes: "The persistence of optical

⁷ Physik. Z., 2, 213 (1901).

⁸ Hatschek: General Discussion, Faraday and Physical Soc. (H. M. Stationery Office, 1920).

strain after the disappearance of all mechanical stress seems capable of explanation by the foregoing theory (p. 132) in that if a molecule be removed by solution from a distorted fibril and then replaced by reprecipitation it will have given up its share of the stress. In this way when all the molecules in the fibril have been replaced the whole of the stress in the fibril will have disappeared, but the fibril will still retain its distorted form." Sheppard and McNally say: "It was shown by Hatschek that the optical anisotropy of gelatin jellies produced by stress does not decrease with the mechanical relaxation of the stress but remains, frequently, at the value corresponding to the first application of the stress. Hatschek has pointed out that this must be due to a permanent rearrangement of inner structure. This is in agreement with the view that gelation involves a condensation of ultimate molecular entities, which is followed by reorientation on application of stress."

In view of the peculiar character of the optical anisotropy produced by deformation it appeared of interest to examine whether gelatin gel under stress became anisotropic as regards its mechanical properties, such as the Young's modulus or tensile strength. It is of course easy to test these points on specimens which have undergone permanent deformation, and I have shown⁹ by direct test that the tensile strength of a cylinder which had received a permanent elongation of 4% was over 80% higher than that of a cylinder in the original state. No such method is available for discovering possible anisotropy in the reversibly deformed gel, and the only way of doing so appears to be the observation of the lenticular gas bubbles produced in the gel while stressed.

I first drew attention to these bubbles in 1914¹⁰ and then put the question whether the equatorial planes of the bubbles showed any orderly arrangement or were orientated at random—a question which I attempted to answer by the somewhat laborious procedure of determining the angles of inclination of a large number with an orthogonal system of coordinates. The problem fortunately assumed a simpler shape when I returned to it in 1929⁹ and can now be stated as follows: We imagine, for the sake of simplicity, a small spherical bubble as existing in the isotropic gel and increase the pressure in it. A pressure will be reached when the tensile strength is exceeded and the gel is torn. The position of the fracture, *i.e.*, its angles with a system of axes, will be just as uncertain as will be the position of the break in a rod broken by tensile stress, and it therefore follows at once that if a large number of such bubbles is examined, their orientation must be a random one. It also follows at once that, if the tensile strength should be a minimum in one direction, the gel would be split at right angles to this direction, *i.e.*, *the equatorial planes of the bubbles will be at right angles with the direction of minimum tensile strength*. As bubbles can readily be produced in a gel while it is reversibly deformed, this affords a means of discovering possible anisotropy during that period.

The gels used for these trials consisted of: 10 gm gelatin (air dry), 1 gm sodium hydrogen carbonate and 100 gm of water. Cylinders were cast in the same way as the specimens for the determination of Young's modulus by

⁹ Hatschek: Kolloid-Z., 49, 244 (1929).

¹⁰ Hatschek: Kolloid-Z., 15, 226 (1914).

compression. The gas bubbles were formed by allowing the following solution to diffuse into the gel: 16 gm glacial acetic acid and 30 gm crystallized sodium acetate made up to one litre with water (about 0.26 *N* in acid and 0.22 *N* in acetate). The acetate is sufficient to repress the swelling due to the acid almost entirely: a specimen weighing 22.390 gm before immersion weighed 23.535 gm after diffusion was complete, the increase amounting to only 5%.

Gas bubbles were produced in cylindrical specimens during reversible and irreversible elongation and during reversible and irreversible compression. The specimens for the latter were, as already stated, cast so as to have plane end faces; for permanent deformation they were compressed in small screw presses and kept in a saturated atmosphere for 4-7 days. For studying the

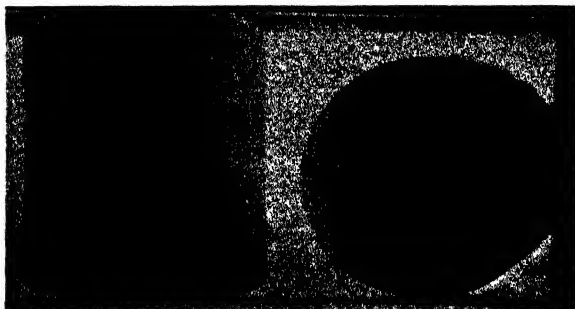


FIG. 6

Gas Bubbles in (right) reversibly, (left) irreversibly compressed gelatin gel

effect of reversible deformation the cylinders were compressed between glass plates in small wooden or ebonite frames and at once placed in the acid-acetate mixture. Fig. 6 shows the orientation of the bubbles during reversible (right) and after irreversible compression (left).

Specimens for tension were attached to beech wood blocks and stretched in ebonite frames; for reversible deformation they were at once placed in the acid-acetate mixture, while for irreversible deformation they were also kept for 4-7 days in a saturated atmosphere, then released from the wood blocks and placed in the acid-acetate solution. The results, which have been obtained quite uniformly on a large number of specimens, are as follows:

In *reversibly elongated* and *irreversibly compressed* cylinders the equatorial planes of the bubbles are *perpendicular* to the axis, *i.e.*, the *tensile strength* is a *minimum* in the direction of the axis.

In *irreversibly elongated* and *reversibly compressed* cylinders the equatorial planes of the bubbles are *parallel* to the axis, *i.e.*, the *tensile strength* is a *minimum* in directions at right angles to the axis.

The results can be put more generally and without reference to the shape of the specimen by saying that during *reversible deformation* the direction of *minimum tensile strength* is that in which the *linear dimension* has been *increased*, and after *irreversible deformation* that in which the *linear dimension* has been *reduced*. For both types of deformation therefore the direction of

minimum tensile strength during reversible deformation is at right angles with that after irreversible deformation. In the interval of time during which the deformation changes from one type to the other, therefore, some rearrangement of the structure must take place.

For the moment I will not insist on the difficulty of bringing this result into harmony with the optical anisotropy, which remains unaltered during the transition from reversible to irreversible deformation. It appeared to me to be possible, that deformation, as it obviously causes a rearrangement, might sensibly affect the diffusion velocity, *i.e.*, that this might also become different in different directions. A series of experiments, which are here published for the first time, was therefore undertaken to test this point.

The principle and technique are again quite simple. If diffusion into a gel is allowed to take place through an orifice which may be regarded as a point, the boundary of the diffusion zone at any time is a sphere, provided the gel is isotropic for diffusion. Should the velocity in different directions become different as a consequence of deformation, the boundary surface would become oblate or prolate. As a sharp boundary of the zone is essential, it is necessary to use a diffusing solution which produces a precipitate with some solute present in the gel. I have found the formation of lead chromate the most suitable reaction for the purpose. The gels are made with a 1% solution of lead acetate—which incidentally acts as an excellent antiseptic—and a concentrated solution of potassium chromate allowed to diffuse into them.

Cylindrical test pieces with smooth plane ends, cast in the manner described earlier in this paper were used. A mask of transparent celluloid about 1.4 mm thick is squeezed to one end face so as to exclude air, the removal of which is easily checked by the absence of total reflection. A countersunk hole, 1 to 1.5 mm dia. drilled in the centre of the mask serves as the "point" source of diffusion: a drop of saturated potassium chromate solution is placed on it, care being taken not to trap an air bubble in the hole, and a few small crystals of the salt placed in it to keep the solution saturated.

The arrangement can be used for studying diffusion both during reversible and irreversible compression. For the former purpose an ebonite plate having a circular opening of 15 to 20 mm diameter is placed over the mask, to give sufficient access to the hole when the drop of solution is placed on it, and the whole is then compressed in a suitable framework. A diffusion zone of sufficient size can be obtained in about 48 hours in an 8 percent gel: if this were to be taken out of restraint, it would show an immediate small recovery followed by a still smaller one which continues for 24 hours or more. The diffusion zone formed during compression would therefore be distorted and, though its original profile could of course be found by calculation, a simpler way is to place the specimen and the press containing it in an atmosphere of formaldehyde, the supply of which can be so regulated that the specimen is hardened completely before being taken out.

Permanently deformed specimens were obtained by compressing cylinders in small screw presses kept in a saturated atmosphere for varying periods. On removal of the restraint there is an immediate partial recovery, followed

by a further one, which is smaller in amount and takes a time of the order of 24 hours to complete itself. The following figures for cylinders of 9 percent gel give an idea of these effects:

Cylinders of 9% gel compressed to the following fractions of their original length

A	B	C	D
83.3%	81.3%	77.3%	74.7%

Removed from restraint after 48 hours. Percent of original length immediately on removal

89.2	87.2	85.9	84.8
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24 hours later

89.9	90.4	89.6	87.7
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The slight irregularity of the first two values in the last row suggests that the time for both the immediate and for the final recovery may be a function of the original stress, *i.e.*, the time may have been insufficient for complete recovery. The point, while interesting and deserving of investigation, is not material to the present enquiry, as the length of compressed specimens was always checked at intervals, and diffusion was not begun until it had remained constant for at least 24 hours.

The results are somewhat surprising or at any rate appeared so to me. *The diffusion zone both in reversibly and irreversibly deformed gels always is perfectly spherical.* This was established by the examination of a large number of specimens which were cut in half when the diffusion zone, as seen through the celluloid mask, had attained a diameter of at least 20 mm. Such a cross-section is shown in Fig. 7.

The gel therefore, as far as the *velocity of diffusion* in it, or its permeability, is concerned, *remains isotropic both during reversible and after irreversible deformation.*

The effects of deformation on various properties of gelatin gel are therefore:

1) Gels become optically anisotropic on deformation and remain so while the deformation becomes irreversible, the amount and "sign" of the anisotropy remaining substantially unaltered while the stress disappears.

2) Gels become anisotropic in respect of tensile strength, but the direction of minimum tensile strength during reversible deformation is at right angles to that after irreversible deformation. *In reversibly deformed gels the direction of minimum tensile strength is that in which the linear dimension of the specimen has been increased, while in permanently deformed gels it is the direction in which the linear dimension has been reduced.*

3) Gels remain *isotropic for diffusion* both during reversible and after irreversible deformation.

A large number of investigators (Sheppard, Poole, Northrop, Kunitz, Lloyd and Pleass) agree in postulating for gelatin a structure consisting of fibrils orientated at random and in assuming that the elastic behaviour of the

gel is simply the elastic behaviour of such a network, the liquid phase playing a part merely in such phenomena as "creep." As the best test of a hypothesis is its application to new phenomena, it will be convenient to examine what effect the deformation of such a structure would have on the three properties studied by me.

The persistent isotropy in regard to diffusion velocity is no doubt easiest of explanation. It may be taken as established that diffusion in gels of low or moderate concentration is not much slower than in the pure dispersion medium; if a fibrillar structure is assumed it must therefore be taken to occupy a comparatively small portion of the total volume. In that case it is easy to understand that deformation would not very materially affect the cross section available in any direction and would accordingly not cause perceptible anisotropy.

The effects of deformation on tensile strength are much more difficult to interpret, and it is necessary to discriminate between reversible and irreversible deformation. The former reduces tensile strength in the direction of dilatation, a result intelligible even without any assumption concerning structure: the material is already stretched in that direction and the additional tensile stress required to cause rupture is smaller.

The converse effect, that after irreversible deformation the tensile strength is greatest in the direction of dilatation must be explained in terms of structure and on the assumption that the tensile strength of the gel, like its elasticity, is merely that of the fibrillar network. The first point to be remembered is that it does not become merely a *relative* maximum, but that the tensile strength of permanently stretched specimens is *absolutely* greater than that of undeformed specimens of equal age. The aggregate cross-sections with a plane perpendicular to the stress can hardly be assumed to increase while deformation becomes permanent: the diffusion experiments, for what they are worth, provide evidence that the passage ways remain equal in all directions. It must however, be borne in mind that, when a structure consisting of fibrils orientated at random is ruptured by tensile stress, the rupture of individual fibrils will be caused by a combination of tensile and shearing stress, the latter prevailing more and more as the angle of the fibril with the direction of stress increases. Now the fibrils must be built up of elements, the name and nature of which are immaterial at the moment; the simplest general structure we can assume is a cylinder built up from equal elements with oblique parallel ends

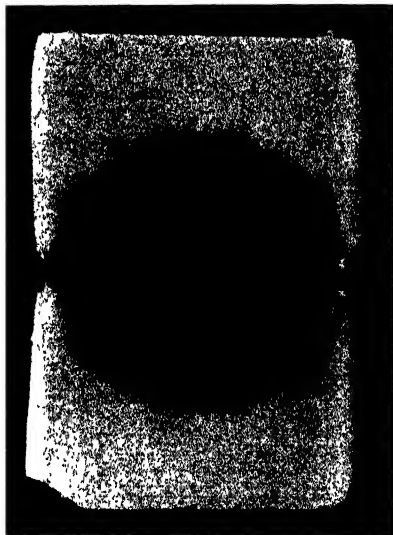


FIG. 7

Diffusion in Cylinder compressed reversibly to 83% of original length. Specimen cut through axis and halves placed together to show the sphericity of the diffusion zone

(Fig. 8a). If the joints are easier to shear than the material of the elements, it is obvious that a rotation of the cylinder through 90° (from a to b) will reduce its resistance to a shearing stress in the direction of the arrow. The assumption that such a rotation occurs is of course purely *ad hoc*, and is an attempt to keep within the theory which ascribes the mechanical properties to a fibrillar network, and to suggest a mechanism consistent with the diffusion isotropy and easily reconcilable with the unchanging optical anisotropy.

Before, however, great weight can be attached to such a hypothesis, much further investigation of the actual transition from reversible to irreversible deformation is required. The gas bubble method gives unambiguous results

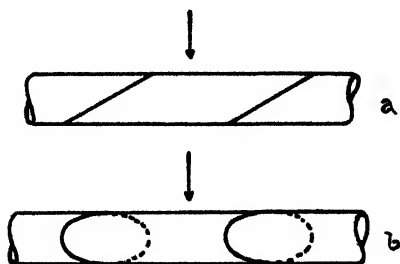


FIG. 8

for the two extreme states, and I have made many attempts to apply it to the intermediate stages. The progress of orientation, however, cannot be traced except by laborious statistical methods which I have not yet found time to apply. An interesting question, which may be settled incidentally, is the following: in the extreme stages the gel is, apparently, uniaxial. Does it become biaxial or isotropic at some stage

during the transition? Since the axes of minimum strength in the extreme states are at right angles to each other, either case would seem to be possible.

It is convenient to discuss at this point the gelatin gel hardened by formaldehyde. The specimens examined contained initially 8 gm and 10 gm of gelatin to 100 gm of water, and the moduli were 283 and 366 gm/cm.² After 165 hours the moduli had increased to 2391 and 4716 gm/cm.² During this time both gels had lost water, and comparison between the natural and hardened gel must be based on the gelatin content of the latter at the time of measurement. The ratios: water/gelatin after 165 hours were 10.27 and 8.38 resp., and the moduli of gels of natural gelatin of these concentrations, obtained by graphical interpretation from the data previously given are 355 and 452 gm/cm.² By the reaction with formaldehyde the modulus of the (originally) 8% gel had therefore increased in the ratio $2391/355 = 6.73$, and that of the (originally) 10% gel in the ratio $4716/452 = 10.42$.

Interpretation of these figures is made difficult by the uncertainty how far they are from equilibrium values, but is not easy even on the assumption, which the graphs seem to support, that the ratio of the moduli at equilibrium does not differ greatly from that at 165 hours. It is not probable that any structure present in the original gel can undergo substantial rearrangement at ordinary temperature; the hardened specimens when examined in polarized light show a certain amount of strain, but no more than is exhibited by gel specimens which have lost the same fraction of their water content by drying in air. Failing rearrangement of structure, the increase in the modulus of the

hardened gel must be due to an increase in the modulus of the fibrillar material. In that event (assuming, of course, saturation with CH_2O) the ratio

$$\frac{\text{Modulus of hardened gel}}{\text{Modulus of natural gel of same gelatin content}}$$

should be the same for all concentrations. This, as has been shown, is very far from being the case, and the hypothesis that the elastic behaviour of the gel is merely the behaviour of an elastic net work seems inadequate. In this connection the considerable loss of water during hardening may be significant. On the basis of accepted theory it may be explained by an increase in the modulus of the net work without a corresponding increase in the osmotic pressure of the liquid phase which is assumed to balance the elastic forces. This may account qualitatively for the loss of liquid, though much further work would be required to determine whether it does so quantitatively; in any event it does not, without some subsidiary hypothesis, provide an explanation of the great difference between the relative increases in the moduli of the two gels.

Problems of equal difficulty are raised by the data—scanty as they are so far—on the elastic behaviour of agar and silicic acid gels. The first thing that requires explanation in terms of structure is the high absolute value of both moduli, and the rapid increase with time exhibited by the modulus of silicic acid gel. This ageing effect also raises the fundamental problem played by water, since the only ready explanation of the increase with time appears to be displacement of water from one phase to the other. With agar there is the further possibility that investigation of the temperature coefficient of elasticity may throw light on this point, and on the mechanism of water retention which in this gel appears at first sight to be radically different from that in gelatin.

While the first approach to the subject thus seems to raise more questions than it answers, I have little doubt that further study of the elastic behaviour of gels, and possibly of their tensile strength, supplemented by diffusion experiments over a large range of conditions, should afford us a deeper insight into their structure than we possess at present.

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X-RAY STUDIES ON THE HYDROUS OXIDES

I. Alumina

BY HARRY B. WEISER AND W. O. MILLIGAN

The addition of a base to a solution of an Al salt gives a highly gelatinous precipitate usually designated as $\text{Al}(\text{OH})_3$. While considerable evidence indicates that the gelatinous mass when first formed is hydrous Al_2O_3 , and not an aluminum-oxide hydrate such as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, a number of older as well as more recent investigations point to the existence of a hydrate or a series of hydrates in the freshly precipitated gel.

A critical survey of the evidence for and against the existence of definite hydrates in precipitated alumina was made 6 years ago.¹ Since that time the situation has been complicated by the interpretation put on vapor pressure and x-ray data obtained more especially by Hüttig and Willstätter. In the present article are given: (A) An historical summary in tabular form of vapor pressure and x-ray data on (1) precipitated alumina and (2) the trihydrate of alumina. (B) An x-ray study of (1) Hüttig aluminas, (2) Willstätter aluminas, (3) precipitated alumina aged at 100° , (4) aged alumina decomposed by heat, (5) alumina formed by the decomposition of hydrated aluminum chloride, (6) alumina formed by the decomposition of gibbsite (7) artificial gibbsite.

A. Historical

(1) *Precipitated Alumina.*

Composition. The precipitate formed by the interaction of NH_4OH and a soluble Al salt will henceforth be designated as precipitated alumina. Different investigators have assigned various formulas to the precipitate dried in different ways. Some typical results are summarized in Table I. It is apparent that while certain investigators, especially van Bemmelen and Shidei, question the existence of hydrates, others, notably Hüttig and Willstätter, believe that a part of the water is chemically bound in the orthodox sense to give definite compounds. The work of Willstätter and of Hüttig will receive critical consideration in the experimental part of this paper.

The vapor pressure data of Shidei on precipitated alumina commands special attention. He treated AlCl_3 solution with NH_4OH , washed the resulting precipitate by decantation several times and then dialyzed it for 11 days at 50° – 60° . The resulting precipitate was free from Cl^- and SO_4^{--} but still contained a trace of ammonia. The vapor pressure curve at constant temperature for this precipitate was determined in a specially designed apparatus. Extreme care was taken to obtain equilibrium values which in some experiments required over 70 days. The curve reproduced in Fig. 1 shows clearly

¹ Weiser: "The Hydrous Oxides" (1926).

TABLE I
Composition of Precipitated Alumina

Investigator	Method of drying	Composition mols H_2O per mol Al_2O_3	Investigator's conclusions
Van Bemmelen ¹	Air-dried	4.3 to 4.5	No definite hydrates except possibly a trihydrate
Carnelley and Walker ²	Air-dried	5	Either no hydrates or a very large number of hydrates
	At 65°	3	
	At 160–200°	2	
	At 250–290°	1	
	At 850°	0	
Allan ³		Precipitated Cold Hot	Composition determined by method of drying
	Air-dried	3.03 2.89	
	Over H_2SO_4	2.020 2.04	
	At 100° C	2.015 1.88	
Guichard ⁴	Air-dried	6.59	The di- and trihydrates exist in the cold precipitate
Hüttig and co-workers ⁵	Aged under varying conditions	3 to 1	A series of definite hydrate are formed
Willstätter and coworkers ⁶	Pptd. and dried under varying conditions	3 to 1	Definite hydrates are formed
Shidei ⁷	Varying pressure	See Fig. 1	No hydrates

that no definite hydrates are formed under the conditions of Shidei's experiments. It was assumed that the water is present in the form of a solid solution in the alumina; but it is more probable that the water is retained by adsorption forces on the surface of finely-divided crystals.

¹ Rec. Trav. chim., 7, 75 (1888).

² J. Chem. Soc., 53, 87 (1888).

³ Chem. News, 82, 75 (1900).

⁴ Bull., (4) 37, 251, 381 (1925); 39, 190 (1926).

⁵ Z. anorg. Chem., 171, 323 (1928); 187, 1 (1930).

⁶ Ber., 56, 149, 1117 (1923); 57, 58, 1087 (1924); 58, 2448, 2458 (1924); 64, 1697 (1931).

⁷ Mem. Coll. Sci. Kyoto, 9a, 42 (1924).

X-Ray Data. A number of investigators have examined precipitated alumina by x-ray diffraction methods. Haber¹ obtained no diffraction effect with a precipitate formed in the cold and air-dried, but observed one broad band in the precipitate from an ultrafiltered alumina sol prepared by Crum's method. He concluded from this that the gel is amorphous when thrown down in the cold but gradually assumes an ordered structure. Frick and Weaver,² on the other hand, observed one broad diffraction band from a precipitate formed at room temperature and a weak pattern from one thrown down at 100°. Böhm³ obtained a well-defined pattern which he described as similar to

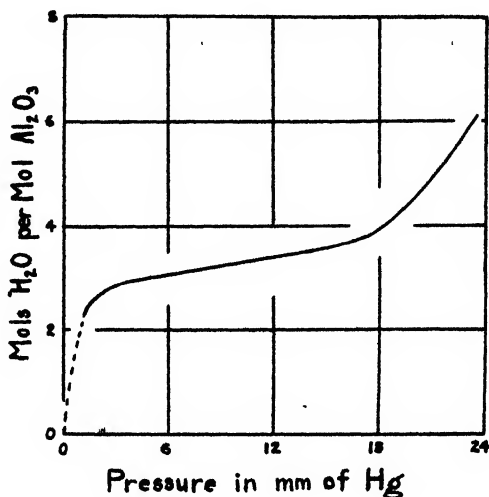


FIG. 1

Vapor Pressure-Composition Diagram for Precipitated Alumina (after Shidei)

some "bauxites" in a precipitate thrown down at 100°. These qualitative observations have been extended by more recent quantitative work which has been summarized in Table II and Fig. 2. Because of the similarity in the x-radiograms from a number of the samples, it is necessary to reproduce only a few of them. The numbers in the last column of the table correspond to the numbers of the x-ray diagrams shown in the figure. It will be noted that all of Biltz and Lehrer's samples yield similar but not identical diffraction effects. Rooksby examined a number of preparations formed with varying concentrations of ammonium hydroxide at both room temperature and at 100°. The x-ray patterns from the several samples were identical except for a slight variation in the width of the lines, showing that the conditions of preparation influence the particle size. The lines were quite diffuse but the positions were the same with the product formed by the thermal decomposition of gibbsite. Further discussion of Rooksby's results will be given in a later section.

¹ Ber., 55, 1727 (1922); Böhm and Niclassen: Z. anorg. Chem., 132, 1 (1920).

² Z. anorg. Chem., 136, 321 (1924).

³ Z. anorg. Chem., 149, 203 (1925).

TABLE II
Precipitated Aluminas used in X-Ray Diffraction Studies

Investigator	Treatment	Composition mols H ₂ O per mol Al ₂ O ₃	No. in Fig. 2
Biltz and Lehrer ¹	Dried:		
	At 100°	1.03	—
	With liquid NH ₃	1.15	—
	With liquid NH ₃	2.995	1
	With acetone	2.88	2
	With liquid NH ₃	2.04	—
	With liquid NH ₃	1.00	3
	With acetone	1.00	—
	With acetone	1.71	—
	With liquid NH ₃	1.49	—
	With liquid NH ₃	1.98	4
	With acetone	3.16	—
	With acetone	2.39	—
	With acetone	2.55	—
	With liquid NH ₃	2.98	5
de Jong ²	precipitated and dried at 40–45°	—	6
	" " " " 100°	—	—
Rooksby ³	Dehydration of Gibbsite at 250°	1	7
	Precipitated at 20°	—	Similar to 7
	" " 100°	—	" " 7

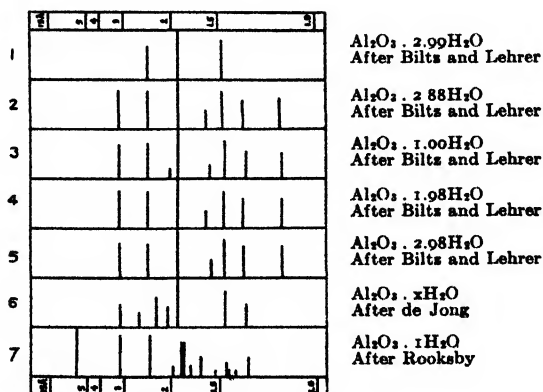


FIG. 2
X-Ray Diffraction Diagrams of Precipitated Aluminas

¹ Z. anorg. Chem., 172, 302 (1928).

² Z. Krist., 66, 303 (1928).

³ Trans. Ceram. Soc. England, 28, 399 (1929).

(2) *The Crystalline Trihydrate.*

The mineral gibbsite occurs in nature in the form of well-defined crystals. The artificial preparation of this compound has been accomplished in a variety of ways. Thus Bonsdorff¹ and Bayer² dissolved alumina gel in KOH and allowed the solution to stand in a closed vessel until crystals appeared. Similarly, Goudriaan³ dissolved Al in NaOH and allowed the solution to

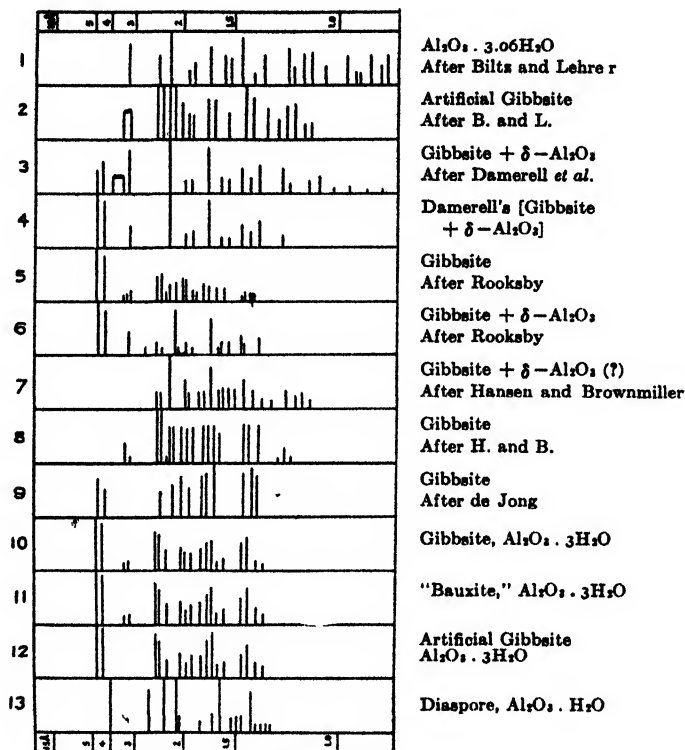


FIG. 3

X-Ray Diffraction Diagrams of Natural and Artificial Gibbsites, etc.

stand in the air, and Fricke⁴ passed CO_2 slowly into cold alkali aluminate solution or slowly hydrolyzed the aluminate by dilution. While the composition of the several preparations corresponds to the formula $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, there is a difference of opinion as to whether the artificial preparations are identical with gibbsite. This point has been investigated by x-ray diffraction methods. The results are summarized in Table III and a number of x-ray diagrams are reproduced in Fig. 3. Except for the results of Biltz and Lehrer, the evidence is fairly conclusive that the artificial preparations are either identical with

¹ Pogg. Ann., 27, 275 (1833).

² Chem.-Ztg., 12, 1209 (1889).

³ Proc. Roy. Akad. Amsterdam, 23, 129 (1921).

⁴ Z. anorg. Chem., 175, 249 (1928); 179, 287 (1929).

TABLE III
Artificial Gibbsite and Similar Preparations

Investigator	Method or sample	X-ray pattern obtained	No. in Fig. 3
Biltz and Lehrer ¹	Precipitated by NH_4OH at 70° and dried with acetone	Unlike gibbsite	1
	Bonsdorff's method	Somewhat like gibbsite	2
Damerell ²	Precipitated alumina aged in cold	Similar to gibbsite	3
Weiser and Milligan	Damerell's sample	Similar to gibbsite	4
Frick and coworkers ³	Slow hydrolysis in cold of alkali aluminate	Identical with gibbsite	—
	Rapid hydrolysis of alkali aluminate	Similar to some "bauxites"—	—
L. H. Milligan ⁴	Bayer's method	Identical with gibbsite	—
Rooksby ⁵	Mineral gibbsite	Gibbsite pattern	5
	Goudriaan's method	Somewhat different from gibbsite	6
Hansen and Brownmiller ⁶	Goudriaan's method	Similar to Rooksby's results	7
	Mineral gibbsite	Gibbsite pattern	8
de Jong ⁷	Mineral gibbsite	Gibbsite pattern	9
Weiser and Milligan	Mineral gibbsite	Gibbsite pattern	10
	Mineral "bauxite"	Gibbsite pattern	11
	Bonsdorff's method	Gibbsite pattern	12
	Goudriaan's method	Gibbsite pattern	12
	Mineral diaspoire	Diaspoire pattern	13

gibbsite or are gibbsite mixed with more or less of a crystalline form of alumina which has been termed $\delta\text{-Al}_2\text{O}_3$ (See experimental part). Our x-radiograms of (1) a mineral gibbsite, (2) a mineral "bauxite" and (3) artificial gibbsites obtained by Bonsdorff's and Goudriaan's methods were identical as nearly as could be determined (Fig. 3: 10, 11, and 12). It is not obvious why the

¹ Z. anorg. Chem., 172, 302 (1928).

² Damerell: J. Phys. Chem., 35, 1061 (1931); Damerell, Hovorka, and White; 36, 1255 (1932); Tartar and Damerell: 36, 1419 (1932).

³ Z. anorg. Chem., 175, 249 (1928); 179, 287 (1929).

⁴ J. Phys. Chem., 26, 247 (1922).

⁵ Trans. Ceram. Soc. England, 28, 399 (1929).

⁶ Am. J. Sci., (5) 15, 225 (1928).

⁷ Z. Krist., 66, 303 (1928).

x-radiograms of Bonsdorff's and Goudriaan's artificial gibbsites obtained by Biltz and Lehrer, Rooksby, and Hansen and Brownmiller should exhibit the differences shown in Fig. 3. As will be pointed out in the section "Synthesis of Gibbsite" in the experimental part of this paper, it is probable that the differences are due in part to variations in the conditions of preparation of the several samples.

B. Experimental

(1) *Preparations according to Hüttig's Procedures.*

Hüttig and coworkers¹ prepared a number of alumina precipitates and studied them by isobaric dehydration and x-ray diffraction methods. The gel freshly precipitated in the cold, appeared to be amorphous and to lose water continuously with increasing temperature. On standing at ordinary temperatures the fresh gel went over gradually into $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. According to Hüttig the transformation was not direct; but a series of crystalline intermediate hydrates between $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was believed to form. Every member of this series of hydrates manifested its individuality by a definite step-like curve.

Hüttig and Kostelitz recognized two more or less separate and distinct ageing processes; (a) gelatinous alumina, which consists of alumina and adsorbed water, reacts with the adsorbed water to form a series of compounds ending with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; (b) a lower alumina hydrate, assumed to be $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore) with adsorbed water, reacts with the adsorbed water giving a series of compounds with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ as the final product. These two processes are represented in Figs. 4 and 5, respectively. In Fig 4 the transformation is from I \rightarrow II \rightarrow III \rightarrow IV in which I represents the non-crystalline $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, II and III, intermediate hydrates and IV, gibbsite. The second process is represented in Fig. 5 in which the changes are from 1 which is the curve for the monohydrate (diaspore) through 2, 3, 4, and 5, the curves for intermediate hydrates, to 6, the curve for gibbsite.

X-radiograms of the several products were found to exhibit differences each from the other. This was likewise interpreted to mean that each was a definite chemical individual intermediate between non-crystalline alumina monohydrate on the one hand and trihydrate on the other.

It is well known that differences in the mode of precipitation of a definite material may influence the particle size and thus the width (sharpness) of the lines on the x-ray diffraction pattern; but differences in the position and relative intensities of the lines require further explanation. The differences in the position may be accounted for as the result of (1) formation of a solid solution with water in varying amounts, (2) experimental errors inherent in the apparatus employed, (3) error in measuring the positions of the lines due to a failure to calibrate the film with a material of known spacings (4) the samples being mixtures rather than pure definite compounds as Hüttig and Kostelitz assumed their intermediate products to be. Of course, no signifi-

¹ Hüttig and Wittgenstein: *Z. anorg. Chem.*, **171**, 323 (1928); Hüttig and Kostelitz: **187**, 1 (1930).

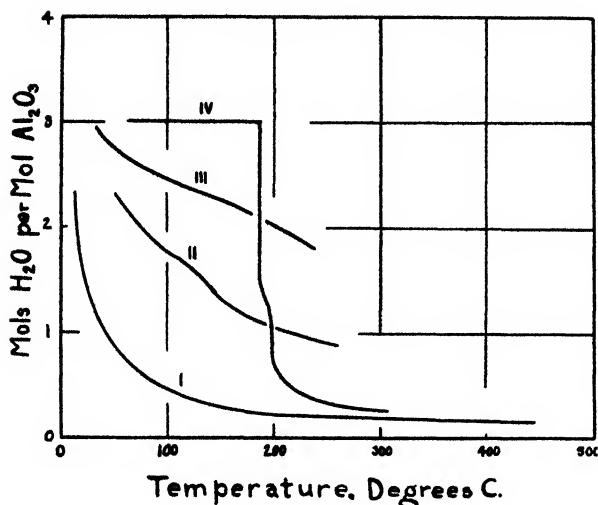


FIG. 4

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, I)

cance can be attached to slight differences in visually estimated intensities. Unfortunately Hüttig's x-ray data are recorded only in chart form on a small scale, and it is altogether impossible to make any accurate comparisons with the results of other people.

Preparation and Treatment of Samples. In the present investigation samples of precipitated aluminas were prepared and aged as nearly as possible in accord with the procedures of Hüttig and Kostelitz. Both the *K* and *L* series of samples were investigated. To prepare the former, one liter of 2 *N* NH_4OH was added with stirring to 90 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 200 cc of

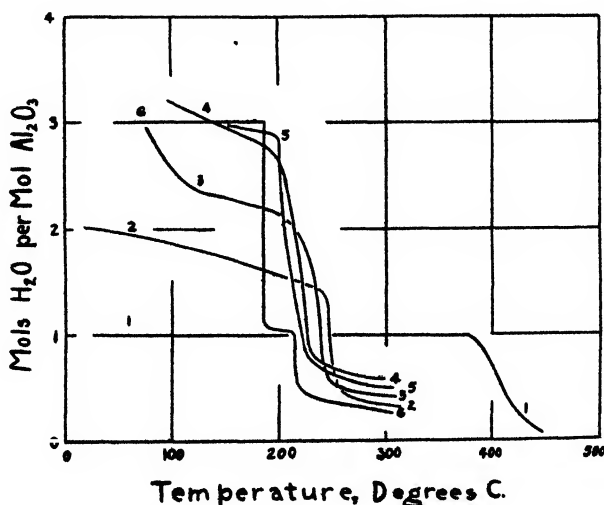


FIG. 5

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, II)

water at room temperature. The resulting hydrous precipitate was placed in 250 cc wide-mouthed bottles and washed ten times by the aid of the centrifuge using 200 cc portions of water. At the conclusion of the washing, the gel was almost chloride free and sol formation had begun. The sample was divided into five parts and aged as shown in Table IV.

The *L* samples were made by adding 48 cc of 25% NH_4OH at 48°C to 548 cc of a solution containing 118 g $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$ and 37.6 g of NH_4Cl . The resulting precipitate was washed as above described and four samples were aged as given in Table IV.

TABLE IV
Ageing of Precipitated Aluminas

Samples	Method of Ageing
K_1 and L_1	In a closed desiccator over 10% H_2SO_4 ; K_1 , 15 weeks and L_1 , 18 weeks
K_1''	Same as K_1 for 29 weeks
K_2 and L_2	In the open air but protected from dust for 27 weeks
K_3 and L_3	In a closed desiccator for 31 weeks
K_4 and L_4	Over water in a closed desiccator for 22 weeks

X-Ray Examination. The samples above described were air-dried, powdered, and placed in a thin nonex capillary tube, one end of which contained a sample of very pure NaCl which was used to calibrate the film. X-ray diffraction patterns were obtained with the General Electric x-ray diffraction apparatus. The results are given in Table V, and the diagrams of the x-radio-grams are shown in Fig. 6. The interplanar spacings $d_{hkl}/n = D$ are expressed in Ångstrom units; *I* represents the relative, estimated intensity on such a scale that 10 is the most intense line. In the figure the x-ray pattern of gibbsite and of what we have termed $\delta\text{-Al}_2\text{O}_3$, are included for the purpose of reference.

It is impracticable to discuss these data until the evidence for the existence of $\delta\text{-Al}_2\text{O}_3$ is given. It is significant however that Hüttig's *K* samples formed in the cold are all quite similar and are probably mixtures of gibbsite with $\delta\text{-Al}_2\text{O}_3$. The *L* samples formed at higher temperature give patterns almost identical with that of $\delta\text{-Al}_2\text{O}_3$ except L_3 which is similar to the *K* samples. It is not apparent why the gibbsite structure should have started in but one of the *L* samples. However, the temperature of formation was not sufficiently high to preclude this possibility and one might expect it to happen occasionally. It is altogether probable that if L_3 has been aged a longer period, it too would have changed in part into gibbsite.

(2) *Preparations according to Willstätter's Procedures.*

Samples of several aluminas were made according to the procedures of Willstätter and coworkers and were examined by the x-ray diffraction method.

Preparation of Samples. A. One liter of a solution containing 100 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 100° was added to one liter of 6 *N* NH_4OH at 50° with

TABLE V

K_{α}'		K_{β}'		K_{γ}		K_{α}		L_{α}		L_{β}		L_{γ}		L_{δ}	
D	I	D	I	D	I	D	I	D	I	D	I	D	I	D	I
4.65	10	4.76	9	4.75	8	4.79	10	4.75	10	4.75	10	4.79	10	3.18	7
4.32	10	4.31	9	4.36	8	4.34	10	4.39	9	4.39	9	4.39	9	2.36	8
3.22	3	3.18	4	3.19	2	3.19	4	3.22	5	3.22	5	3.22	5	1.85	10
2.36	4	3.46	2	2.39	2	2.47	2	2.47	3	2.47	3	2.47	3	1.43	6
2.22	10	2.37	3	2.22	10	2.37	3	2.37	3	2.37	3	2.37	3	1.31	4
2.00	2	2.26	1	1.99	1	2.26	1	2.22	10	2.22	10	2.22	10	2.22	10
1.87	2	2.22	10	1.90	1	2.22	10	2.01	2	2.01	2	2.01	2	2.01	2
1.71	6	1.99	1	1.789	1	2.00	2	1.89	2	1.89	2	1.89	2	1.89	2
1.55	1	1.885	1	1.721	5	1.89	1	1.72	8	1.72	8	1.72	8	1.72	8
1.44	5	1.770	1	1.436	3	1.77	1	1.64	1	1.64	1	1.64	1	1.64	1
1.38	3	1.709	7	1.390	2	1.72	7	1.60	1	1.60	1	1.60	1	1.60	1
1.33	4	1.639	1	1.65	1	1.65	1	1.56	1'	1.56	1	1.56	1	1.56	1
1.21	1	1.589	1	1.60	1	1.60	1	1.44	3	1.44	3	1.44	3	1.44	3
1.16	1	1.550	1	1.55	2	1.55	2	1.39	2	1.39	2	1.39	2	1.39	2
1.13	1	1.431	4	1.44	3	1.44	3	1.33	2	1.33	2	1.33	2	1.33	2
		1.389	3	1.39	3	1.39	3	1.21	1	1.21	1	1.21	1	1.21	1
		1.327	4	1.33	4	1.33	4	1.13	2	1.13	2	1.13	2	1.13	2
		1.204	2	1.21	2	1.21	2								

vigorous stirring, after which steam was passed into the mixture for 5 hours, adding more ammonia from time to time. The resulting precipitate was washed free from sulfate and chloride by ordinary decantation and finally by the aid of the centrifuge. A portion of the sample was dried over P_2O_5 for 30 days and then contained 21.72% water. Willstätter and Kraut found a composition approximating $Al_2O_3 \cdot 2H_2O$ for a similar sample dried over H_2SO_4 .

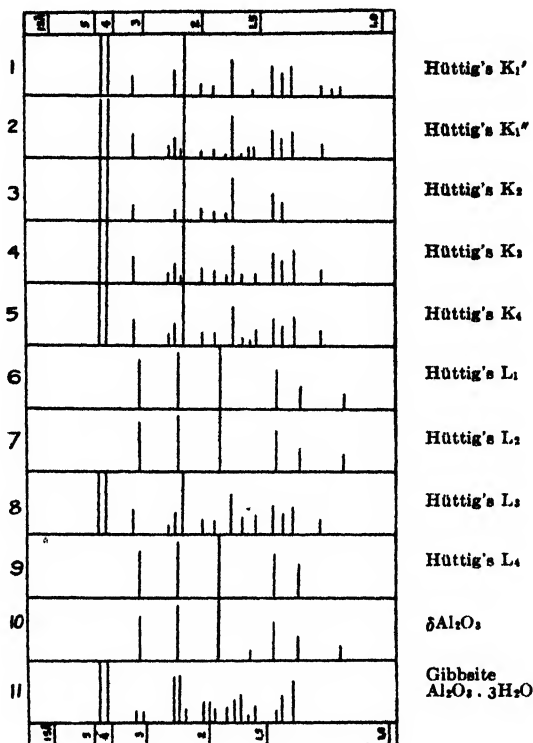


FIG. 6

X-Ray Diffraction Diagrams of Precipitated Aluminas prepared according to Hüttig's Procedures

B. This preparation was precipitated like A, but instead of passing in steam, it was heated on a steam bath for 30 minutes at 65° , then washed nearly free from sulfate and chloride.

D. About 65 g of alumina (calculated as $Al(OH)_3$) were dissolved in a solution of 70 g of KOH in 450 cc of water. The resulting solution was filtered, diluted to 5 liters, and CO_2 passed in rapidly. After thorough washing the sample was dried over P_2O_5 for 30 days.

New A. Willstätter, Kraut, and Humme¹ have recently modified the procedure for preparing the A sample which is claimed to give the definite hydrate $Al_2O_3 \cdot 2H_2O$. A sample was made according to this procedure: A solution of

¹ Ber., 64, 1697 (1931).

250 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in 750 cc of water was warmed to 48° and poured rapidly with vigorous mechanical stirring into 2.5 liters of 15% by weight NH_4OH also at 48° ; the temperature rose to about 50° . The resulting mixture was stirred for 30 minutes, and diluted to 12 liters with distilled water. The precipitate was washed by decantation 4 times after which 1 liter of 15% NH_4OH was added, and stirred for 5 minutes, followed by dilution to 12 liters with distilled water. The washing by decantation was continued until peptization began. About 2 days were required for these operations in accordance with the requirements of Willstätter. The resulting precipitate was then washed with acetone and ether. Samples were dried, A_1 in vacuum, A_2 over P_2O_5 in vacuum, and A_3 at 110° in air.

X-Ray Examination. X-radiograms were made of the 6 samples above described. The position and relative intensities of the lines in the several samples are shown in Table VI and the diagrams for two of the samples only are reproduced in Fig. 7 (5 and 6). It is evident that all of Willstätter's samples formed by precipitation in the hot have the same crystal structure which is that of $\delta\text{-Al}_2\text{O}_3$. The D sample obtained by rapid hydrolysis of aluminate in the cold gave an x-radiogram in which no lines could be detected.

TABLE VI

X-Ray Data for Willstätter's Preparations

A		B		D		New A_1		New A_2		New A_3	
D	I	D	I	D	I	D	I	D	I	D	I
3.16	7	3.15	5								
2.34	8	2.36	7					2.35	6		
1.85	10	1.85	10	General		1.85	10	1.85	10	1.85	10
		1.61	0.1								
1.43	8	1.43	8			1.43	7	1.43	7	1.43	8
1.31	6	1.32	6	Blackening				1.31	5		
1.13	2	1.13	1								

(3) Ageing of Precipitated Alumina at 100° .

Since a survey of reported work indicates that different products are obtained on ageing hydrous alumina in the hot and in the cold, the following systematic procedure was carried out: 200 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was dissolved in 500 cc of water and 125 cc of 15 N NH_4OH was added with vigorous stirring. A sample containing the suspended oxide was removed at once and the remainder was heated to boiling under a reflux condenser. The boiling was continued several weeks, samples being removed from time to time and washed and dried according to the following procedure: Each sample was washed 7 times by the aid of the centrifuge with 50 cc portions of distilled water followed by 5 washings with 50 cc portions of acetone and then dried at 50° . No significance is attached to this particular procedure but it was followed with all samples so that the various compositions are comparable. Willstätter believes that washing with acetone removes all of the adsorbed water, leaving

only chemically combined water. This appears to be definitely in error. However, in the present experiments washing with acetone was used as a convenient method of removing much of the water without the necessity of heating to a high temperature which might decompose definite hydrates, assuming they were present. After drying according to the above procedure the composition was determined and x-radiograms were made. The relationship between the age of sample and water content of the precipitate is given in Table VII and shown graphically in Fig. 8.

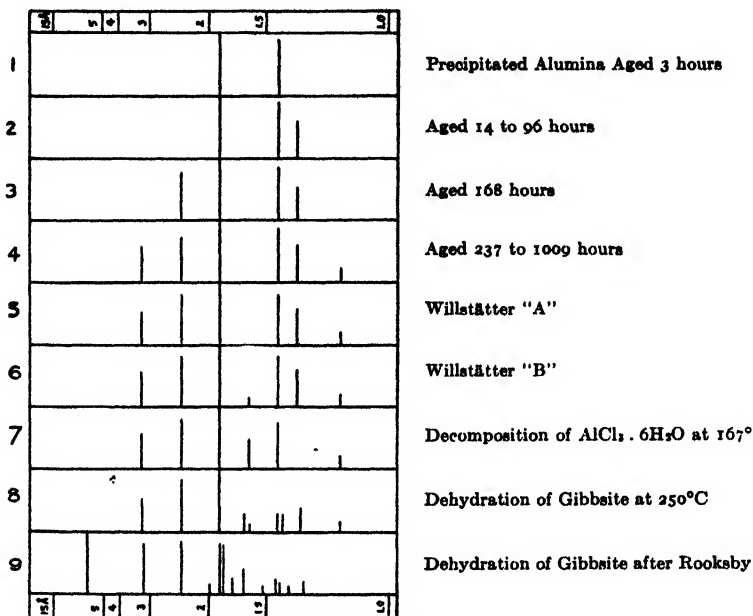


FIG. 7

X-Ray Diffraction Diagrams of Precipitated Aluminas prepared in Various Ways

TABLE VII

Age and Composition of Precipitated Alumina

Age hours	Composition % water	Numbers in Table 8 Fig. 7		Age hours	Composition % water	Numbers in Table 8 Fig. 7	
0	74.73	1	—	96.5	24.15	7	2
1	—	2	—	168	—	8	3
3	40.89	3	1	237	22.51	9	—
14.5	—	4	2	335	—	10	—
24	34.65	5	2	504	—	11	—
72	26.88	6	2	1009	19.35	12	4

The x-ray diffraction data are given in Table VIII and Fig. 7. The results are quite conclusive. The precipitate is amorphous when first formed but ageing in the hot gradually causes a transformation to the crystalline form which shows the same lines on the x-radiogram as Willstätter's A and B samples.

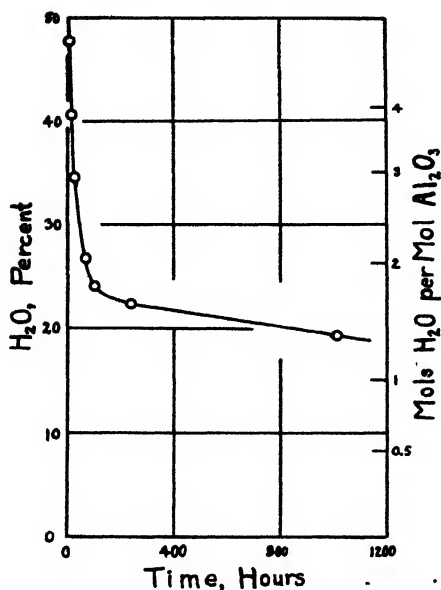


FIG. 8

Time-Composition Curve of Precipitated Alumina aged at 100°C.

TABLE VIII
X-Ray Diffraction Data for Alumin aged at 100°

1		2		3		4		5		6	
D	I	D	I	D	I	D	I	D	I	D	I
General		General		1.85	10	1.84	10	1.84	10	1.84	10
blackening		blackening		1.43	10	1.43	9	1.43	9	1.43	9
						1.32	5	1.33	5	1.33	5

7		8		9		10		11		12 and 12a	
D	I	D	I	D	I	D	I	D	I	D	I
1.84	10	2.38	8	3.15	6	3.15	5	3.16	5	3.18	5
1.43	9	1.84	10	2.34	7	2.33	7	2.33	7	2.36	8
1.33	5	1.43	9	1.85	10	1.85	10	1.85	10	1.85	10
		1.33	5	1.43	9	1.435	8	1.43	8	1.43	8
				1.32	5	1.326	5	1.32	5	1.13	2
				1.14	2	1.14	2	1.13	1		

(4) Dehydration of Alumina aged at 100°.

Since all the samples described in the preceding paragraph were treated with acetone and dried at 50°, it was thought desirable to dry some of these at higher temperatures and thereby reduce the water content. Thus sample 12 having a composition 19.35% water when dried at 50° was heated for about 3 hours at 160° (sample 12a) at which temperature the composition became 10.38%, which corresponds to $\text{Al}_2\text{O}_3 \cdot 0.65\text{H}_2\text{O}$. X-ray examination showed

that the crystal structure had not changed, the results for 12 and 12a being identical. It is obvious therefore that sample 12a, and therefore 12, cannot be diasporite or an isomer of diasporite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$); but must be either a lower hydrate such as $\text{Al}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$, or alumina with adsorbed water. In order to help decide this point, it is necessary to compare the x-radiogram from 12 with those obtained from anhydrous alumina.

Polymorphism of Alumina. $\delta\text{-Al}_2\text{O}_3$. It has been demonstrated that four polymorphic forms of alumina exist: (1) $\alpha\text{-Al}_2\text{O}_3$, which occurs in nature as corundum and has been prepared artificially by heating ordinary alumina to 1800° ;¹ (2) $\beta\text{-Al}_2\text{O}_3$, prepared by allowing molten $\alpha\text{-Al}_2\text{O}_3$ containing 0.5% MgO or 5% Na_2O to cool slowly; and (3) $\gamma\text{-Al}_2\text{O}_3$, formed by heating precipitated alumina in the neighborhood of 900° ,⁴ and (4) $\zeta\text{-Al}_2\text{O}_3$, prepared by allowing molten $\alpha\text{-Al}_2\text{O}_3$ containing 5% Li_2O to cool slowly.^{5,6}

In 1928 Parravano and Montoro⁷ reported the formation of another modification of alumina by heating $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ for 15 days. Biltz, Lemke, and Meisel⁸ called this alleged new modification $\delta\text{-Al}_2\text{O}_3$. However in 1929 Parravano and Onorato⁹ reported a serious error in the 1928 paper. "The spectrum reported in the work cited and attributed to be from alumina at 250° was due to an exchange of samples."

While Parravano's statement disposes of his $\delta\text{-Al}_2\text{O}_3$, this does not mean that another polymorphic form does not exist. It will be recalled that precipitated alumina aged for many hours at 100° , gradually assumed a definite crystalline structure. Upon heating to 160° nearly all the water was driven off. It is most probable that this material is actually a polymorphic modification of Al_2O_3 which has been designated $\delta\text{-Al}_2\text{O}_3$. Attempts were made to dry completely a sample of $\delta\text{-Al}_2\text{O}_3$, but it was found that heating to higher temperatures starts the transformation to the γ -form, before the water is entirely driven off. It is probable that the last trace of water stabilizes the δ -form in somewhat the same manner as the β -form is stabilized by small amounts of Na_2O and MgO .

For purposes of comparison the x-ray diffraction patterns of the α , β , γ , δ , and ζ modification of alumina are given in chart form in Fig. 9. There can be no doubt that each of the five samples possesses a crystal structure entirely different from the others.

¹ Davey: *Phys. Rev.*, (2) 15, 333 (1920); 21, 716 (1923); Maugin: *Compt. rend.*, 178, 785 (1924); Pauling and Hendricks: *J. Am. Chem. Soc.*, 47, 781 (1925).

² Rankin and Merwin: *J. Am. Chem. Soc.*, 38, 568 (1916).

³ Stillwell: *J. Phys. Chem.*, 30, 1444 (1926).

⁴ Ulrich: *Norsk. Geol. Tidskr.*, 8, 115 (1925); Hansen and Brownmiller: *Am. J. Sci.*, (5) 5, 225 (1928); Biltz, Lemke, and Meisel: *Z. anorg. Chem.*, 186, 373 (1930).

⁵ Barlett: *J. Am. Ceramic Soc.*, 15, 361 (1932).

⁶ The experiments of Barlett concerning $\zeta\text{-Al}_2\text{O}_3$ have been repeated and the results confirmed.

⁷ *Atti. accad. Lincei*, (6) 7, 885 (1928).

⁸ *Z. anorg. Chem.*, 186, 373 (1930) cf. Bragg, Gottfried, and West: *Z. Krist.*, 77, 255 (1931).

⁹ *Atti. accad. Lincei*, (6) 10, 475 (1929).

(5) *Thermal Decomposition of Aluminum Chloride.*

In view of the error in Parravano and Montero's report, experiments were carried out to determine, if possible, what form of alumina results on decomposing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. In the first experiment a 5 g sample of salt was placed in an electric oven at 150° . In 10 hours the temperature rose to 250° and the sample was maintained at this temperature for 2 hours. X-ray examination showed the resulting product to be amorphous. A second sample prepared by heating 17 hours at 225° and a third by heating at 250° for 30 days likewise proved to be amorphous. It was then decided to carry out the dehydration

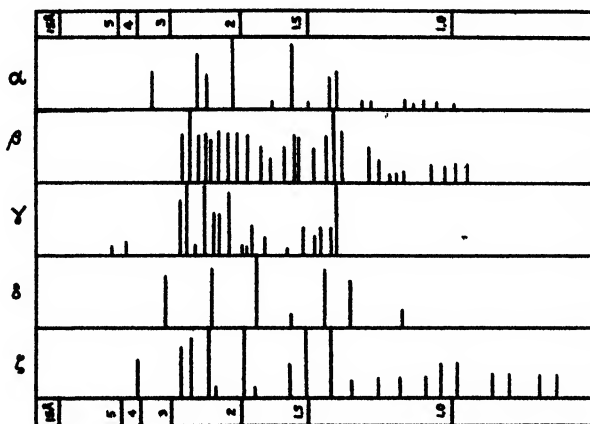


FIG. 9

X-Ray Diffraction Diagrams of α , β , γ , δ and ζ - Al_2O_3

at a lower temperature since a higher temperature favors the transformation to γ - Al_2O_3 . Accordingly, a sample was heated for 72 hours at 165 - 170° . This treatment was insufficient to decompose the hydrate completely; hence the sample was washed with hot water until nearly free from chloride and dried at 60° . X-ray examination showed that a crystalline product resulted which was identical with δ - Al_2O_3 as shown diagrammatically in Fig. 7 (7).

(6) *Thermal Decomposition of Gibbsite.*

Gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, starts to decompose on heating to a temperature in the neighborhood of 200° . (5) Rooksby obtained an x-radiogram of the product formed by thermal decomposition at a temperature of 250° . Under these conditions the composition of the product was represented by the formula $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Since the x-radiogram is different from that of the mineral diaspore, Rooksby thought he had prepared an isomer of diaspore. On examination, the x-radiogram showed such a marked similarity to that of δ - Al_2O_3 , that Rooksby's experiment was repeated. The x-radiogram is shown in Fig. 7 (8), together with those for δ - Al_2O_3 (1-7), and Rooksby's alleged hydrate (9). There is no doubt that the several preparations are identical in crystal structure.

(7) *Synthesis of Gibbsite.*

In the historical portion of this paper was included the diagram for the x-ray pattern of an artificial gibbsite which we prepared (Fig. 3, 12). The sample was made in the following way: To a solution of 56.1 g of KOH in 300 cc of water were added 10 g of Al strips, a little at a time to avoid frothing and heating. The resulting solution was filtered, placed in a stoppered flask, and allowed to stand. Upon examination about 30 days later, the bottom of the flask was covered with a micro-crystalline powder. This material was carefully washed, and dried at 60° and submitted to x-ray examination. The results obtained are given in Table IX and in Fig. 3 (12). For purposes of comparison the data for samples of the minerals "bauxite," gibbsite, and diaspore are likewise given in Table IX and Fig. 3 (10, 11, and 12).

The above method of synthesizing gibbsite is similar to that of Goudriaan. A sample prepared by Bonsdorff's method which is almost the same as Goudriaan's, gave an x-radiogram with the same spacings and intensities. It

TABLE IX
X-ray Data for Gibbsite and Diaspore

10 Gibbsite mineral		11 "Bauxite" mineral		12 Gibbsite artificial		13 Diaspore mineral	
D	I	D	I	D	I	D	I
4.85	10	4.85	10	4.85	10	4.00	10
4.34	9	4.34	9	4.36	8	2.57	8
3.31	1	3.31	1			2.34	10
3.12	1	3.12	1			2.13	10
2.45	7	2.45	7	2.45	6	2.08	2
2.38	7	2.38	7	2.38	6	1.82	1
2.26	1	2.26	1	2.26	3	1.71	2
2.17	3	2.17	3	2.17	3	1.63	10
2.04	3	2.04	3	2.04	3	1.54	1
1.990	2	1.990	2	1.985	3	1.50	2
1.907	2	1.907	2	1.911	3	1.47	2
1.798	3	1.798	3	1.795	3	1.40	8
1.741	4	1.741	4	1.741	3	1.38	1
1.681	5	1.681	5	1.680	4	1.34	1
1.642	0.1	1.642	0.1			1.32	1
1.580	1	1.580	1			1.29	1
1.448	4	1.448	4	1.448	4		
1.404	6	1.404	6	1.404	5		
1.352	2	1.352	2				
1.312	1	1.312	1				

will be recalled that Rooksby obtained different x-radiograms from samples made by those two methods and neither was identical with that of gibbsite. As already pointed out the reason for this is not obvious; but it is probable that he allowed the temperature to rise in the course of the preparation and so obtained δ - Al_2O_3 mixed with gibbsite in varying proportions.

Discussion of Results

From the experiments above described and from the earlier observations of Haber, Frick, and Weaver, and others, it is evident that alumina, freshly precipitated by the interaction of cold solutions of ammonia or alkali and a soluble aluminum salt, is either amorphous or contains such extremely minute crystals that it gives no x-ray diffraction pattern. When the gelatinous precipitate is allowed to age in the hot a crystalline phase appears which gives gradually, an x-ray diffraction pattern identical with that from aluminas obtained by the thermal decomposition of gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, at 250° and from the thermal decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 170° . Long continued ageing causes the crystals to grow as evidenced by the increase in number and sharpness of the lines on the x-ray pattern. Thus, by referring to Table VIII and Fig. 7 it will be seen that the gel aged for one hour gives a pattern showing only general scattering; but after three hours two rather broad bands appear. Continuing the process for several days finally results in a product which yields a pattern quite similar to the one resulting from the dehydration of gibbsite at 200 – 250° . As the material dehydrates no change is noted in the position of the lines showing that the gel is not a solid solution of alumina and water. The gel is therefore hydrous alumina, that is, alumina with adsorbed water, or a hydrous alumina hydrate.

According to Rooksby, the product formed by the thermal decomposition of gibbsite at 250° is $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which gives a different x-radiogram from the mineral diasporé. Rooksby believes that the alleged hydrate from gibbsite is an isomer of diasporé. This conclusion is in error since the x-ray pattern of an aged precipitated alumina having the composition $\text{Al}_2\text{O}_3 \cdot 0.65\text{H}_2\text{O}$ is identical with that obtained with alumina from gibbsite. This pattern is different from the patterns obtained with α - Al_2O_3 , β - Al_2O_3 , γ - Al_2O_3 , and ζ - Al_2O_3 . It is concluded therefore that the product formed by (1) ageing precipitated alumina in the hot (b) decomposition of gibbsite at 250° and (c) decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 170° is a new polymorphic form of alumina which we have termed δ - Al_2O_3 . The possibility that the so-called δ - Al_2O_3 is an alumina hemihydrate has not been definitely excluded but the evidence is against this point of view. In the first place, the data given in Table VII and Fig. 8 for the relation between composition and time of ageing at 100° shows that the precipitated gel loses water in the manner characteristic of hydrous oxides. In the next place, the vapor pressure-composition curve obtained by the precise measurements of Shidei (Fig. 1) gives no indication of the formation of alumina hemihydrate or of any other hydrate, in his preparation. Since his preparation was made by hot dialysis of precipitated alumina, he was working

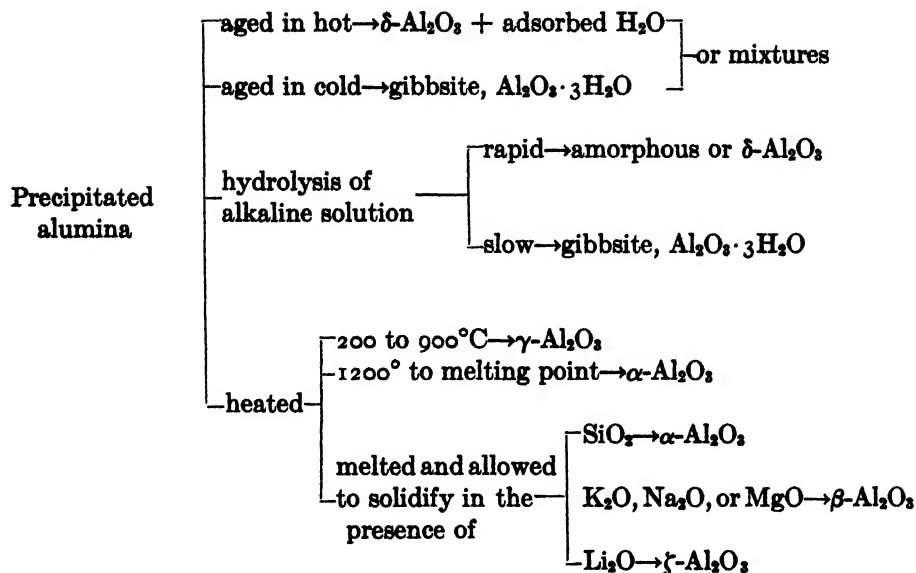
with a product formed by essentially the same procedure which we have found most favorable for the formation of $\delta\text{-Al}_2\text{O}_3$. The obvious conclusion is that the product we have called $\delta\text{-Al}_2\text{O}_3$ is not a hemihydrate.

The evidence from vapor pressure data and especially from x-ray diffraction data does not support the view of Hüttig and Willstätter that precipitated alumina can form a series of hydrates by ageing under suitable conditions. The various preparations of these authors are either $\delta\text{-Al}_2\text{O}_3$ or a mixture of $\delta\text{-Al}_2\text{O}_3$ and gibbsite. The formation of the former is favored by precipitation at high temperature and ageing at high temperature, while the formation of the latter is favored by precipitation and ageing in the cold. In any event the original precipitated gel is hydrous $\delta\text{-Al}_2\text{O}_3$. Under favorable conditions the $\delta\text{-Al}_2\text{O}_3$ first formed changes to gibbsite, the extent of the change being determined by the treatment of the sample.

Summary

The results of this investigation are as follows:

1. X-ray diffraction studies have been carried out on aluminas precipitated under widely varying conditions in order to determine what definite hydrates of alumina exist.
2. The evidence indicates that there are but two alumina hydrates: (1) gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, both natural and artificial, and (2) diaspor, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
3. Precipitated alumina aged at 100° has been found by x-ray diffraction methods to be a new form of alumina, which has been termed $\delta\text{-Al}_2\text{O}_3$, with adsorbed water. It has not been prepared free from adsorbed water but a composition $\text{Al}_2\text{O}_3 \cdot 0.65\text{H}_2\text{O}$ has been obtained without transformation to the $\gamma\text{-Al}_2\text{O}_3$ taking place. The so-called $\delta\text{-Al}_2\text{O}_3$ cannot be a monohydrate (Rooksby), but the possibility that it is a hemihydrate has not been definitely excluded, although the evidence is against this hypothesis.
4. Samples prepared according to the procedures of Hüttig and co-workers were found by x-ray diffraction methods to be either $\delta\text{-Al}_2\text{O}_3$ or a mixture of $\delta\text{-Al}_2\text{O}_3$ and gibbsite, instead of a series of definite hydrates as Hüttig believed.
5. Samples prepared by the methods of Willstätter and co-workers were found by x-ray studies to be either $\delta\text{-Al}_2\text{O}_3$ or amorphous Al_2O_3 with adsorbed water, instead of a series of hydrates as Willstätter believed.
6. Artificial gibbsites prepared by the methods of both Bonsdorff and Goudriaan give x-ray diffraction patterns identical with the mineral gibbsite.
7. The product formed by the thermal dehydration of gibbsite below 250°C is $\delta\text{-Al}_2\text{O}_3$ and not an isomer of diaspor as Rooksby assumed. $\delta\text{-Al}_2\text{O}_3$ is also formed by the thermal decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.
8. The existence of $\zeta\text{-Al}_2\text{O}_3$ recently announced by Barlett, has been confirmed.
9. The various transformations of precipitated alumina may be tabulated in the following diagram:



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X-RAY STUDIES ON THE HYDROUS OXIDES

II. Stannic Oxide

BY HARRY B. WEISER AND W. O. MILLIGAN

The question of the so-called stannic acids and the existence of definite hydrates of stannic oxide have been the subject of repeated investigations from the time of Berzelius to the present. The colloidal nature of the so-called stannic acids was investigated by van Bemmelen,¹ and by Mecklenburg² who concluded that the α and β acids were both hydrous oxides differing from each other in the size of the particles. This same conclusion was reached by one of us³ ten years ago. Investigations made at that time showed that there was no definite dividing line between the two preparations, and that the β oxide consisted of the larger particles. Gutbier, Hüttig, and Döbling⁴ concluded from pressure-temperature curves that no definite hydrates⁵ were formed. The x-ray diffraction patterns of their various samples as well as those of Mecklenburg which had aged for several years, showed that the original hydrous oxide was apparently amorphous and that the aged products exhibited a gradual formation of a crystal lattice identical with the mineral cassiterite, SnO_2 . X-radiograms made by Yamada⁶ of several different preparations,⁷ all revealed a structure identical with the anhydrous stannic oxide. Further x-radiograms of the so-called α and β stannic acids were made by Posnjak⁸ who demonstrated clearly that the structure of both is identical with the anhydrous oxide; and that the difference in the two oxides is due to a difference in particle size, the β being the larger. This is in accordance with the observations of Mecklenburg and of Weiser. Hydrous SnO_2 was dried in a vacuum over P_2O_5 by Forster⁹ who concluded from x-ray data that the products obtained had the structure of cassiterite. X-radiograms of the fresh gel and the products resulting from the ageing and heating of colloidal SnO_2 were obtained by Böhm.¹⁰ His published photographs show clearly the gradual increase in particle size from the original hydrous oxide to the anhydrous SnO_2 , the lattice in all cases remaining identical with that of cassiterite.

In view of all the apparently conclusive evidence that is available, it would appear that the question of the nature of the so-called stannic acids should be

¹ "Die Absorption," 54 (1910).

² Z. anorg. Chem., 74, 207 (1912).

³ Weiser: J. Phys. Chem., 26, 654 (1922).

⁴ Ber., 59, 1232 (1926).

⁵ Cf., however, Willstätter and Kraut: Ber., 59, 2541 (1926).

⁶ J. Chem. Soc. Japan, 44, 210 (1923).

⁷ Rose: Pogg. Ann., 75, 1 (1848); Engel: Ann. Chim. Phys., (3) 12, 463 (1844); Graham: Pogg. Ann., 123, 538 (1864); Schneider: Z. anorg. Chem., 5, 82 (1894); Zeigmondy: Ann., 301, 361 (1898); Collins and Wood: J. Chem. Soc., 121, 441 (1922).

⁸ J. Phys. Chem., 30, 1073 (1926).

⁹ Physik. Z., 28, 151 (1927).

¹⁰ Kolloid-Z., 42, 283 (1927).

considered a settled one; but such is not the case. In a recent investigation Thiessen and Koerner¹ claim that a stannic oxide gel prepared by the slow hydrolysis of stannic ethylate gives pressure-temperature and composition-temperature curves that indicate the formation of a series of hydrates. From pressure-composition data the following hydrates are claimed: $2\text{SnO}_2 \cdot 5\text{H}_2\text{O}$; $\text{SnO}_2 \cdot 2\text{H}_2\text{O}$, $4\text{SnO}_2 \cdot 7\text{H}_2\text{O}$ and $2\text{SnO}_2 \cdot 3\text{H}_2\text{O}$ and from temperature-composition curves; $\text{SnO}_2 \cdot \text{H}_2\text{O}$ and $2\text{SnO}_2 \cdot \text{H}_2\text{O}$. X-radiograms of the several preparations were made, but no definite results were obtainable by this method. It was claimed that the lattice undergoes a slight expansion as the water content decreases;² but that the "strong diffuse blackening" of the film renders impossible the making of exact measurements.

Experimental

In view of the theoretical significance of the existence or non-existence of a series of SnO_2 hydrates, it is the purpose of the present paper to consider (1) the dehydration of stannic oxides at temperatures which are said to give definite hydrates; and (2) the examination of these reputed hydrates by x-ray diffraction methods.

I. The Thermal Dehydration of Hydrus Stannic Oxide.

A. Stannic Oxide prepared by Thiessen and Koerner's Method

Preparation of Oxide. The stannic oxide was prepared according to the procedure outlined in detail by Thiessen and Koerner. Sodium ethylate made by adding metallic sodium to absolute alcohol was allowed to react with an anhydrous SnCl_4 solution in absolute alcohol in accord with the following equation: $\text{SnCl}_4 + 4\text{NaOC}_2\text{H}_5 \rightarrow \text{Sn}(\text{OC}_2\text{H}_5)_4 + 4\text{NaCl}$. All reactions were carried out with extra precautions to prevent the entrance of water vapor into the apparatus or solutions. The resulting mixture of stannic ethylate and NaCl was digested on a water bath, and finally the NaCl was filtered off. An amount of the alcoholic solution of ethylate equivalent to 25 g of anhydrous SnO_2 was added to 5 liters of absolute alcohol. The resulting solution was allowed to stand with occasional stirring in a flask with a neck 5 cm in diameter. Moisture from the air hydrolyzed the stannic ethylate, the process being complete in 26 days. The gelatinous precipitate of SnO_2 was filtered off, washed with 1 liter of 96% alcohol in 100 cc portions, dried with suction on a filter paper, and kept in a glass-stoppered bottle until used.

Rate of Dehydration. The SnO_2 gel made by the above method consists of SnO_2 , alcohol, and water. Thiessen and Koerner obtained a composition-temperature curve by heating a sample at definite temperatures for 15 minutes over CaCl_2 . The resulting curve is shown in Fig. 1. The breaks in the curve are indicative of the formation of the definite hydrates $\text{SnO}_2 \cdot \text{H}_2\text{O}$ and $2\text{SnO}_2 \cdot \text{H}_2\text{O}$.

It would not be expected that an equilibrium state would result from heating the samples for only 15 minutes, and Thiessen and Koerner give no data to

¹ Z. anorg. Chem., 195, 83 (1931).

² Cf. Forster: Physik. Z., 28, 151 (1927).

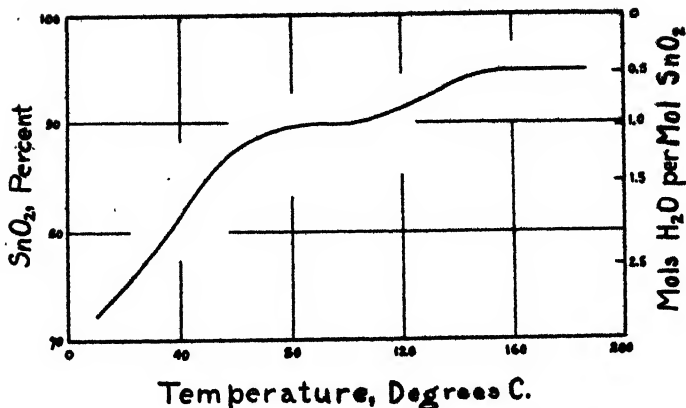


FIG. 1

Temperature-Composition Curve of Stannic Oxide (after Thiessen and Koerner)

show whether or not this is the case. It was thought desirable to determine the time required for equilibrium at a given temperature before proceeding to obtain the composition-temperature curve. To do this a sample was placed in an electric oven with the temperature adjusted to 50°C. The sample was removed at intervals, allowed to cool, weighed, and the heating continued. The resulting curve showing the relation between composition and time of heating, is given in Fig. 2. It will be observed that about 8 hours is required to attain equilibrium at the temperature stated. As would be expected, equilibrium is established more rapidly at higher temperatures; thus at 160°, 2 or 3 hours is sufficient.

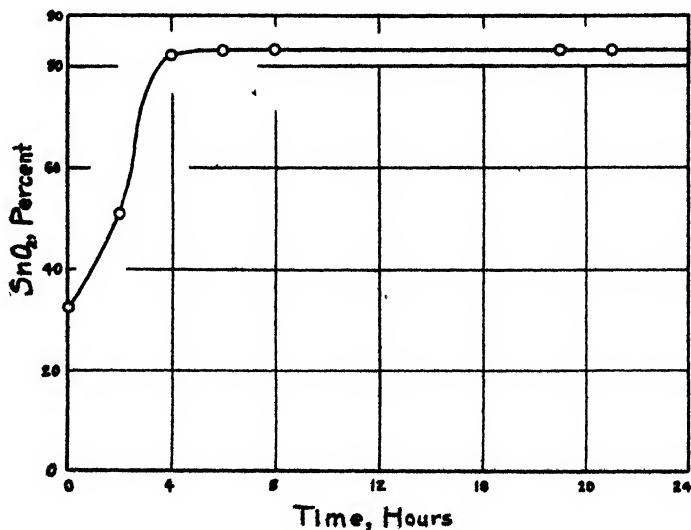


FIG. 2

Rate of Dehydration of Stannic Oxide at 50°C

The form of the time-composition curve is what would be expected from a material containing water and a little alcohol: the rate of drying is quite rapid at first and then falls off, decreasing to a relatively low value before the composition becomes constant. This means that, at first, alcohol and some of the water comes off followed by the greater portion of the water leaving the last trace of water which, as is well known, is very difficult to remove.

The Composition-Temperature Curve. In the light of the above experiments a composition-temperature curve was obtained, taking care to heat the sample at each temperature for at least 12 hours to ensure the establishment of equilibrium. Two samples were taken: the first was allowed to cake into a lump as the heating proceeded, and the second was pre-dried enough to allow it to be powdered. The samples were placed in weighing bottles, and heated to constant weight over calcium chloride at a definite temperature, after which the temperature was raised and the heating continued as before. The dehydration was carried out in a thermo-regulated electric oven, the temperature of

TABLE I
The Thermal Dehydration of Thiessen and Koerner's SnO_2

Temperature °C	Not powdered		Powdered	
	Weight of sample g	SnO_2 %	Weight of Sample g	SnO_2 %
39.6	0.9073	83.25		
40.6	0.9069	83.29		
48.4	0.8997	83.95		
56.3	0.8933	84.56		
60.2	0.8899	84.88		
63.6	0.8857	85.28		
67.8	0.8753	86.29	0.3996	86.13
69.8	0.8735	86.47	0.3989	86.28
74.5	0.8707	86.75	0.3971	86.67
78.6	0.8690	86.92	0.3964	86.82
81.6	0.8674	87.08	0.3953	87.06
85.7	0.8671	87.11	0.3950	87.13
90.0	0.8654	87.28	0.3943	87.29
95.4	0.8637	87.45	0.3935	87.46
100.4	0.8598	87.85	0.3916	87.89
104.7	0.8575	88.09	0.3908	88.07
110.0	0.8549	88.35	0.3894	88.38
116.0	0.8540	88.45	0.3889	88.50
120.0	0.8536	88.49	0.3888	88.52
123.5	0.8531	88.54	0.3887	88.54
132.3	0.8510	88.76	0.3870	88.93
143.2	0.8465	89.23	0.3847	89.46
154.0	0.8423	89.68	0.3833	89.79
202.0	0.8283	91.19	0.3780	91.05

which remained constant within 0.5° . For temperatures below 100° a thermometer was used that had been calibrated against a standard thermometer checked by the Bureau of Standards. Above 100° an accurate thermometer was employed which had been checked at points below 100° against the standard thermometer. The results obtained are given in Table I and in Fig. 3.

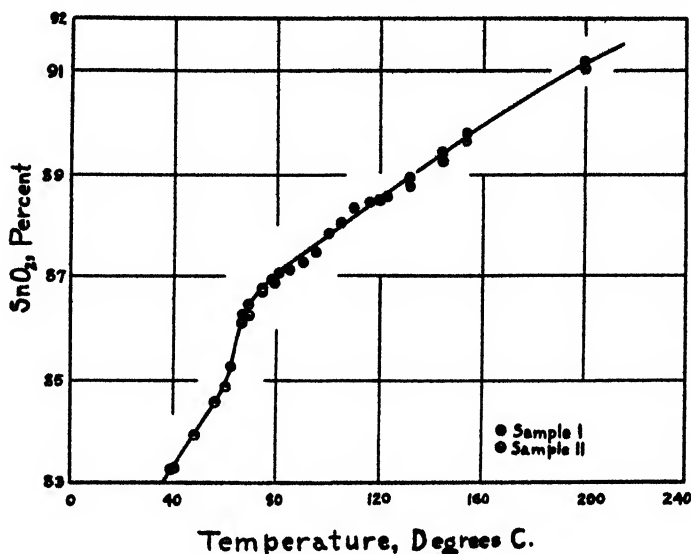


FIG. 3

Temperature-Composition Curve of Stannic Oxide prepared by Hydrolysis of Stannic Ethylate

B. Alpha and Beta Stannic Oxides

For purposes of comparison dehydration curves were obtained for samples of the so-called α and β stannic oxides. A sample of α oxide was prepared by the addition of a slight excess of ammonium hydroxide to a solution of SnCl_4 . The resulting gelatinous precipitate was washed by centrifuging, and finally

TABLE II
The Thermal Dehydration of Alpha and Beta SnO_2

Temperature °C	Alpha		Beta	
	Weight of sample g	Loss in weight %	Weight of sample g	Loss in weight %
39.6	1.8620	0.0	3.7966	0.0
49.0	1.7980	4.33	3.7395	1.50
59.4	1.7267	7.27	3.6398	4.13
69.1	1.6944	8.95	3.5863	5.54
80.3	1.6698	10.32	3.5422	6.70
89.6	1.6511	11.33	3.5166	7.38
99.6	1.6317	12.42	3.4938	7.98

air-dried until it could be powdered. The β oxide was prepared by treating pure metallic tin with concentrated HNO_3 , washing and drying the resulting product in the air. The dehydration of both samples was carried out according to the procedure given above. The results are given in Table II and in Fig. 4. The percentage loss in weight of Thiessen and Koerner's stannic oxide was calculated at each temperature and the results shown in the third curve of Fig. 4.

The significance of the curves obtained from the various preparations will be discussed after a consideration of the results found by an x-ray examination of the alleged hydrates of Thiessen and Koerner.

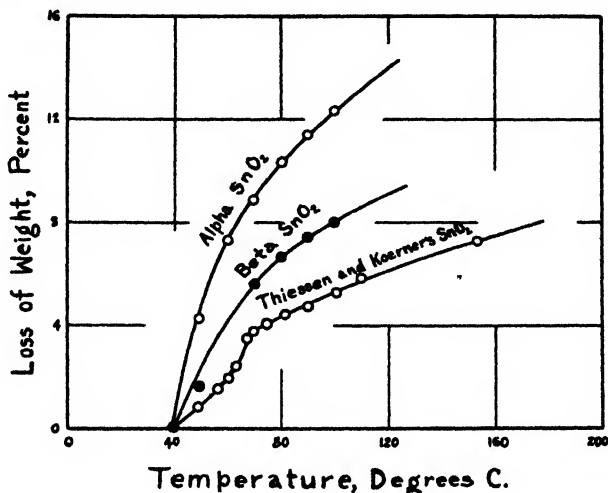


FIG. 4

Temperature-Composition Curves of the So-called Alpha and Beta Stannic Oxides

II. X-Ray Examination of Thiessen and Koerner's Stannic Oxide.

Separate samples of SnO_2 , prepared by the method of Thiessen and Koerner were heated to temperatures that should give definite hydrates according to the composition-pressure and composition-temperature curves of these investi-

TABLE III
X-Ray Diffraction Data for Dehydrated SnO₂

[illegible]

gators. The following temperatures were chosen: 25° , 36° , 50° , 90° , and 160° . Specimens of the heated samples were sealed in tubes of "nonex" glass (a special glass made of materials of low atomic weight) and x-radiograms made by the powder method in the usual manner, using a General Electric x-ray diffraction apparatus. In each case the pattern of NaCl was obtained on the same film for purposes of calibration. The interplanar spacings and the visually estimated relative intensities are given in Table III and in chart form in Fig. 5. The spacings are in Ångstrom units and the intensities on such a scale that the most intense line is designated as 10.

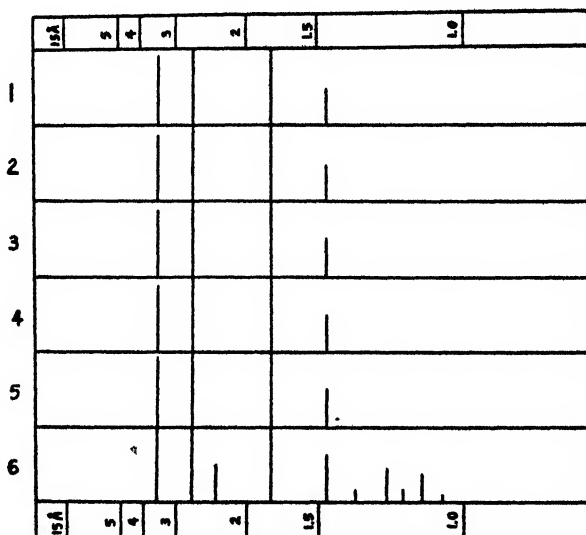


FIG. 5

X-Ray Diffraction Patterns for Stannic Oxides: Thiessen and Koerner's Preparations dehydrated at (1) 25°C , (2) 36°C , (3) 50°C , (4) 90°C , and (5) 160°C , (6) The Mineral SnO_2 .

Discussion of Results

Composition-temperature curves of hydrous stannic oxide have previously been obtained by Carnelley and Walker¹ and by van Bemmelen.² The smooth curves obtained by these investigators were quite similar to those for the α and β stannic oxides, shown in Fig. 4. The curve obtained from the preparation of Thiessen and Koerner is similar except for a change in its direction at about 60 – 70° . The reason for this is obvious when it is recalled that the material consists of SnO_2 , water, and a little alcohol. The odor of alcohol is still apparent in a sample that has been heated to 40° and there is no question but that traces of alcohol persist at least up to the boiling point. As has been seen, samples of SnO_2 containing only water give a smooth, continuous curve. Samples containing alcohol but no water would be expected to give a curve of

¹ J. Chem. Soc., 53, 83 (1888).

² "Die Absorption," 54 (1910).

the same type but would reach the maximum sooner. In the case under consideration, in which both loss of alcohol and loss of water are superimposed on the same curve, the two effects added together algebraically would be expected to give a curve of the shape found experimentally to hold. Since Thiessen and Koerner did not allow sufficient time for equilibrium to be established, the breaks in their curves are without significance so far as hydrate formation is concerned. This point has already been adequately discussed by Posnjak in connection with similar results of Willstätter and Kraut.

Since the crystal structure of all the products formed at various temperatures is identical with the mineral cassiterite, SnO_2 , with respect to the position and relative intensity of the lines on the x-radiograms, no definite hydrates of SnO_2 are actually formed. The only difference in the diffraction effects is that the size of the particle, as indicated by the width of the lines in the products obtained by dehydration, are smaller than those which compose the mineral cassiterite. It should be noted from Table III and Fig. 5, that the interplanar spacings do not change (within the expected experimental error for such wide lines) with varying amounts of water, as would be the case if the SnO_2 and water formed a solid solution. This shows that the water must be adsorbed on the surface of the finely-divided crystals.

Hydrous SnO_2 , whether in the so-called α or β form or as prepared by the method of Thiessen, consists of very small crystals of SnO_2 which adsorb water or both water and alcohol in the Thiessen preparation. When the latter material is dehydrated, at temperatures up to about $60\text{--}70^\circ$ most of the alcohol and some of the water is driven off; at temperatures above this point where little alcohol is left, the dehydration proceeds in a uniform manner as in the case of the familiar α and β preparations.

Thiessen and Koerner found that the general blackening of the film upon which the x-ray diffraction patterns were recorded precluded accurate measurements, and concluded that the method was not suitable for distinguishing the presence or absence of hydrate formation. No such difficulties are encountered, however, when the proper exposure is made, and a special glass of low atomic weight is used. It is true, of course, that the broad, diffuse lines cannot be read with the accuracy obtainable on sharper lines; nevertheless all lines recorded in Table III are clearly visible on the original negatives.

Summary

The results of this investigation are as follows:

1. Hydrous stannic oxide has been prepared by the hydrolysis of stannic ethylate according to the method of Thiessen and Koerner, who claim that a series of definite hydrates of SnO_2 results from the thermal dehydration of this material.
2. Composition-temperature curves have been obtained under conditions that ensure the establishment of equilibrium. The curves are smooth indicating the absence of hydrate formation. Breaks in the curves of Thiessen and

Koerner were due to their failure to allow sufficient time for equilibrium to be established under a given set of conditions.

3. X-radiograms of preparations obtained by dehydration at definite temperatures, show that no definite hydrates are actually formed, the several products consisting of SnO_2 of varying particle size with varying amounts of adsorbed water. This confirms the observations of Gutbier, Hüttig, and Döbling; Posnjak; Yamada; Weiser; and others.

4. The claim of Thiessen and Koerner, that the x-ray diffraction method is not suitable for determining the presence or absence of hydrates, has been shown not to be valid; on the contrary, when the proper precautions are taken the results are definite and conclusive.

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X-RAY STUDIES ON THE HYDROUS OXIDES

III. Stannous Oxide

BY HARRY B. WEISER AND W. O. MILLIGAN

Historical

Anhydrous Stannous Oxide. Stannous oxide was prepared by Berzelius¹, by the addition of K_2CO_3 in excess to a solution of stannous salt. Gay Lussac² obtained a hydrous precipitate with NH_4OH , and dehydrated this material by boiling under water until a black SnO appeared. Ditte³ stated that the presence of NH_4OH prevented the alleged transformation to the anhydrous oxide; however if the NH_3 is boiled off, the dehydration proceeds. An excess of alkali, insufficient to dissolve the oxide, favors the transformation.⁴ Sandall⁵ prepared a black form of SnO by grinding fused $SnCl_2$ with $Na_2CO_3 \cdot 10H_2O$. The blue-black oxide of Berzelius became brownish-green when pounded or ground. Upon heating, an olive-green color developed.⁶ Frémy evaporated a dilute solution of NH_4Cl in which precipitated SnO was suspended; when crystals of NH_4Cl appeared, the hydrous material was said to change to a cinnabar-colored powder which was transformed to greenish-brown upon rubbing with a hard body. Roth⁷ obtained a red oxide by digesting the hydrous material with CH_3COOH ; but Bury and Partington⁸ were unable to prepare this form. Frankel and Snipischsky⁹ added $NaOH$ to a solution of $SnCl_2$; the white precipitate was transformed into a blue powder when boiled for several hours on a bath of saturated $NaCl$ solution. Frémy believed that three modifications of SnO exist, namely: (1) the blue-black, crystalline oxide made by digesting hydrated SnO with excess alkali, (2) the olive-green powder obtained by heating the black modification, and (3) the cinnabar-colored powder resulting from the slow evaporation of a suspension of precipitated SnO in a dilute NH_4Cl solution.

Precipitated Stannous Oxide. The precipitate obtained by the interaction of solutions of stannous salts and an alkali has been formulated $Sn(OH)_2$, although there is no evidence that such is the case. Proust¹⁰ found that an excess of K_2CO_3 gave a white precipitate containing 5% water. Schaffner¹¹ believed

¹ Gilbert's Ann., 42, 284 (1812); Pogg.'s Ann., 28, 443 (1833); Ann. Chim. Phys., (1) 87, 50 (1813); (2) 5, 149 (1817).

² Ann. Chim. Phys., (2) 1, 40 (1816).

³ Ann. Chim. Phys., (5) 27, 145 (1882); Compt. rend., 94, 792, 864 (1882).

⁴ Nordenskjöld: Pogg. Ann., 114, 612 (1861).

⁵ Phil. Mag., (3) 12, 216 (1838).

⁶ Frémy: Ann. Chim. Phys., (3) 12, 460 (1844); 23, 385 (1848).

⁷ Ann., 60, 214 (1846).

⁸ J. Chem. Soc., 121, 1998 (1922).

⁹ Z. anorg. Chem., 125, 235 (1922).

¹⁰ J. phys., 51, 173 (1800); 61, 338 (1804); Ann. Chim. Phys., (1) 28, 213 (1798); Nicholson's J., (1) 2, 515 (1798); (2) 14, 38 (1806).

¹¹ Ann., 51, 174 (1844).

that NH_4OH gave a basic salt. K_2CO_3 was said to give a precipitate that had the composition $2\text{SnO} \cdot \text{H}_2\text{O}$ when dried below 80°C .

TABLE I

Precipitated from SnCl_2 by	Color	Dried	Composition % water
NaOH	Yellow tinge	Vacuum, P_2O_5 , 14 da	7.11
Na_2CO_3	Yellow tinge	$\text{CaCl}_2 + \text{P}_2\text{O}_5 + \text{KOH}$, 14 da	8.54
NH_4OH	Yellow, dried	P_2O_5	8.32
NH_4OH (CO_2 atmosphere)	Yellow, dried	P_2O_5	8.82
Na_2CO_3 (CO_2 atmosphere)	Yellow tinge	Vacuum, P_2O_5 , 14 da	7.4
$\text{NaOH} + \text{Na}_2\text{CO}_3$	—	110°C air bath	2.5

Ten years ago Bury and Partington¹ investigated the hydrous precipitate prepared in several ways; the various methods used are listed herein as Table I. These investigators concluded that all samples were the same except the last, and that the composition was $3\text{SnO} \cdot 2\text{H}_2\text{O}$. It was observed,² that when precipitated SnO stood in a glass vessel, the portion in contact with the glass darkened. Bury and Partington attributed this to the action of traces of alkali on the surface of the glass, since it is well known that excess alkali favors the transformation to the blue-black oxide. This view was apparently substantiated by the observation that samples kept in silica tubes did not blacken.

Brown and Henke³ treated SnCl_2 solution in a glass cylinder with Na_2CO_3 . The first preparation was white when precipitated and slightly yellow when dried. Subsequent precipitates darkened before washing was complete. The blackening was said to begin along the sides of the glass cylinder in streaks coincident with scratches on the glass caused by a stirring rod. Washing with concentrated HCl had no effect, but treatment with NaOH prevented further blackening of the precipitate. Brown and Henke believed that the first black particles act as catalysts to produce further blackening, but offer no explanation as to the formation of the initial particles. The theory of Bury and Partington would have predicted that treatment with alkali would produce more rather than less blackening. It is probable that some other factor is entering in. This is suggested by Roth's observation that one of his preparations rapidly turned black upon exposure to sunlight.

The present investigation includes (1) an examination of the various modifications of SnO by x-ray diffraction methods in order to determine whether the differences in color and other properties are due to the existence of polymorphic forms of SnO , to varying particle size, or to some combination of these effects; (2) a study of precipitated SnO to find out whether it is a hydrous oxide or a hydrous hydrate; and to determine the conditions that effect the blackening.

¹ J. Chem. Soc., 121, 1998 (1922).

² Cf. Ditte: Loc. cit.

³ J. Phys. Chem., 27, 739 (1923).

Experimental

Anhydrous Stannous Oxide.

A. Blue-black α -SnO. A solution of 25 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 200 cc of water was cleared up with HCl and 20 g of NaOH in 200 cc of water was added. A white or faintly yellow precipitate formed which turned to a blue-black powder upon heating to boiling. This powder was washed thoroughly by decantation and was dried for 18 hours at 110°C .

B. Brownish-green α -SnO. A portion of *A* was ground in an agate mortar; this treatment gave a brownish-green powder.

C. Greyish-green β -SnO. Another portion of *A* was heated in a vacuum in a pyrex tube. At about 550°C the blue-black crystals were transformed to a greyish-green powder.

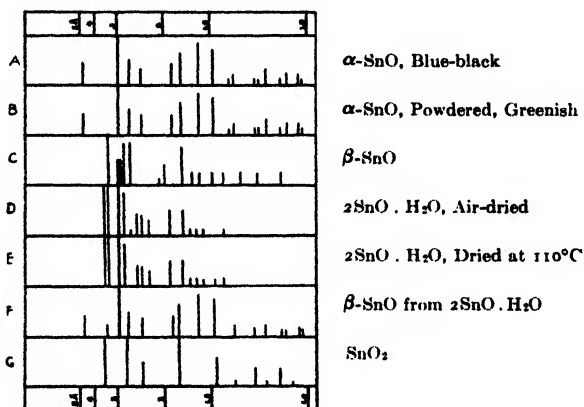


FIG. 1

X-Ray Diffraction Diagrams of Stannous Oxides and Stannous Oxide Hemihydrate

Attempts to prepare the red forms of Roth and of Frémy were unsuccessful, in confirmation of the results of Bury and Partington.

Samples of each of the above described preparations were sealed in nonex glass tubes, and x-ray diffraction photographs were obtained using the General Electric X-Ray Diffraction Apparatus. Pure NaCl was used to calibrate the film. The results are given in Table II and Fig. 1. The interplanar spacings $D = d_{hkl}/n$ are expressed in Ångstrom units; and the relative, estimated intensities, I , are expressed on such a scale that 10 means the most intense line on a given film. The pattern obtained from the α -SnO corresponds to a tetragonal structure of the PbO type¹ with $a_0 = 3.78$ Å and $c_0 = 4.79$ Å. The calculated density is 6.51. The results are almost identical with the values found by Levi,² who obtained $a_0 = 3.77$ Å and $c_0 = 4.77$ Å. The pattern of β -SnO was not studied further. The results indicate that SnO exists in two polymorphic

¹ Dickinson and Friauf: J. Am. Chem. Soc., **46**, 2457 (1924).

² Nuovo Cimento, (8) **1**, 335 (1924); **3**, 114 (1926); cf. Wyckoff: "The Structure of Crystals," 228 (1931).

TABLE II
X-Ray Diffraction Data for Anhydrous and Hydrated SnO

A & B α -SnO		C β -SnO		Sample D $2\text{SnO}\cdot\text{H}_2\text{O}$ Air-dried		E $2\text{SnO}\cdot\text{H}_2\text{O}$ Dried 110°C		F α -SnO from $2\text{SnO}\cdot\text{H}_2\text{O}$	
D	I	D	I	D	I	D	I	D	I
4.79	4	3.38	10	3.53	10	3.52	10	4.79	4
2.96	10	2.99	5	3.32	10	3.32	10	3.37	2
2.68	5	2.92	5	2.99	10	2.98	9	2.97	10
2.40	3	2.88	9	2.82	9	2.79	9	2.68	5
1.890	4	2.66	9	2.64	1	2.51	4	2.40	3
1.787	7	2.08	1	2.51	4	2.40	4	1.90	4
1.595	9	2.02	4	2.40	4	2.27	3	1.795	7
1.482	8	1.769	8	2.27	3	1.925	5	1.595	9
1.369	1	1.675	2	1.925	5	1.771	5	1.489	8
1.336	2	1.595	2	1.776	5	1.691	1	1.339	2
1.220	1	1.496	2	1.690	1	1.624	1	1.221	1
1.195	1	1.414	2	1.625	1	1.575	1	1.168	3
1.165	3	1.294	2	1.572	1	1.466	1	1.100	1
1.099	1	1.204	2	1.406	1	1.405	1	1.074	2
1.072	2	1.096	2					1.026	2
1.027	2							0.993	1
1.018	1							0.899	1
0.992	1							0.882	1
0.932	1							0.847	1
0.900	1							0.838	1
0.879	1							0.802	1
0.872	1							0.750	1
0.850	1								
0.839	1								
0.798	1								
0.749	1								
0.712	1								

forms: α -SnO, the blue-black tetragonal form which is brownish-green when in a finely-divided state; and β -SnO, the greyish-green modification prepared by heating the α -SnO to above 550°C .

Hydrous Hydrated Stannous Oxide.

Stannous oxide hydrate was precipitated from a freshly prepared and filtered HCl solution of SnCl_2 by the addition of NH_4OH . Upon the addition of the NH_4OH the temperature rose from that of the room to about 60°C . The white or faintly yellow colored, hydrous precipitate was washed first with ammonia and then with water by centrifuging at 3000 r.p.m. until peptization began. A very stable sol resulted before the precipitate was chloride free; centrifuging for over an hour at 3000 r.p.m. failed to produce coagulation. Accordingly, further purification was carried out by washing with a super-

centrifuge at 36000 r.p.m. After repeated washing only a trace of chloride remained. The precipitate was then air-dried until it could be powdered, and a sample was placed in a weighing bottle and was dehydrated by heating in an electric oven in a stream of dry nitrogen, which was purified by passing through a heated pyrex combustion tube containing copper freshly reduced by hydrogen from cupric oxide wire. The nitrogen was not rendered completely oxygen free, since continued heating at high temperatures resulted in some oxidation of the oxide. However oxidation is negligible in the temperature range for which results are reported. The isobaric temperature-composition curve that was obtained with three separate samples is plotted in Fig. 2. The compo-

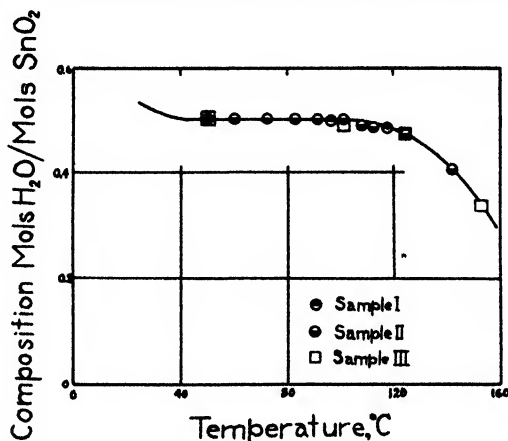


FIG. 2

Composition-Temperature Curve of Stannous Oxide Hemihydrate

sition when dried in the manner described at 50°C was found to be, % SnO: observed 93.70, 93.71, 93.74; calculated for $2\text{SnO} \cdot \text{H}_2\text{O}$, 93.74. It is apparent from the form of the curve that the hydrated SnO has the composition corresponding to the hemihydrate, $2\text{SnO} \cdot \text{H}_2\text{O}$. As the dehydration proceeds, the sample becomes decidedly yellow by the time the temperature reaches 100°; at higher temperatures a grey or green color appears. The change in color from the white or faintly yellow to the permanent deeper yellow, is a continuous one. The nature of this change will be discussed in the second paragraph following.

X-radiograms were obtained for the following samples: *D*, $2\text{SnO} \cdot \text{H}_2\text{O}$, air-dried; *E*, $2\text{SnO} \cdot \text{H}_2\text{O}$, dried at 110°; and *F*, $\alpha\text{-SnO}$ prepared by heating $2\text{SnO} \cdot 2\text{H}_2\text{O}$ to about 400° in a vacuum. The results are given in Table II and Fig. 1. For purposes of comparison, *G*, the pattern of SnO_2 is also included in Fig. 1. It will be observed that the crystal structure of the hemi-hydrate is different from either the $\alpha\text{-SnO}$ or the $\beta\text{-SnO}$, and that the product of thermal decomposition is $\alpha\text{-SnO}$, provided the temperature is kept below 550°C, the transition temperature for the α to β transformation.

Since the x-radiograms for hemi-hydrate dried in the air and at 110° are the same, the change in color from white or faintly yellow to decidedly yellow, can-

not be due to isomerism; but must be due to a change in particle size or physical character. From the width of the lines on the x-radiograms, it appears that the deep yellow material has the larger particles. Thus crystal growth takes place as the hemi-hydrate is heated.

Blackening of Hydrated SnO on Exposure to Light. Stannous chloride in slight excess was treated with NH_4OH in a pyrex flask in the dark. Test tubes were filled with portions of the suspension and stoppered and aged as given in Table III. The samples exposed to light were left in a test-tube rack in ordinary daylight. The others were kept in a closed cupboard in a dark room, and were examined at intervals. Inspection of Table III makes it clear that the

TABLE III

Container	Kept in dark				Exposed to light			
	5 min.	2 hrs.	1 wk.	2 wks.	5 min.	2 hrs.	1 wk.	2 wks.
Soft glass	white	white	white	white	white	grey	green-grey	green
Pyrex	white	white	white	white	white	grey	green-grey	green
Fused silica	white	white	white	white	white	grey	green-grey	green

nature of the containing vessel has little or nothing to do with the darkening; but that it is caused by the action of light. In order to test further the effect of light and the effect of the nature of the surface of the containing vessel, another experiment was carried out. Hydrated SnO was precipitated from a slight excess of SnCl_2 by NH_4OH in a pyrex flask in diffused daylight. Within 5 minutes after precipitation, samples were placed in soft glass cylinders treated as in Table IV.

TABLE IV

Time	Exposed to light				Kept in dark			
	New cylinder washed with		Scratched cylinder washed with		New cylinder washed with		Scratched cylinder washed with	
	HCl	NaOH	HCl	NaOH	HCl	NaOH	HCl	NaOH
5 min.	white	white	white	white	white	white	white	white
15 min.	grey	grey	grey	grey	white	white	white	white
1 da.	green	green	green	green	white	white	white	white
3 da.	green	green	green	green	white	white	white	white
1 wk.	green	green	green	green	white	white	white	white

The coloration begins on the side of the glass nearest the most intense illumination. In each of the above described series of experiments, a portion of each precipitate was made alkaline with NH_4OH and allowed to stand in the light in a pyrex flask. Only slight darkening takes place, and the original white or faint yellow may become slightly deeper. As is well known, a solution of SnCl_2 in dilute HCl hydrolyzes, precipitating out a white, creamy substance upon standing. Since in the experiments described, an excess of SnCl_2 is present, one would expect the same thing to happen; and such is the case. However, there is no danger of confusion as to color, as the deposit forms in a separate thin, upper layer.

Two samples (not included in the tables) one with a slight excess of SnCl_2 and the other with a slight excess of NH_4OH , after standing several weeks, contained some blue-black crystals which were proven by microscopic and x-ray examination to be $\alpha\text{-SnO}$. It is apparent that the blackening process consists of a transformation of the white or faintly yellow $2\text{SnO} \cdot \text{H}_2\text{O}$ first to anhydrous $\alpha\text{-SnO}$ in the finely-divided greenish-brown form, and second to blue-black $\alpha\text{-SnO}$ as the particles increase in size. This dehydration is accelerated by the action of light, especially in the absence of free ammonia. The nature of the containing vessel and its surface is of minor if not of negligible importance. The failure of Bury and Partington to observe darkening in silica was probably due to their use of an opaque vessel.

Summary

The following is a brief summary of the results of this investigation.

1. Stannous oxide has been found to exist in two polymorphic forms: $\alpha\text{-SnO}$ which is blue-black in large crystals and brownish-green when powdered; and $\beta\text{-SnO}$ which is greyish-green. The transition temperature from the α to the β form is approximately 550°C .
2. The crystal structure of $\alpha\text{-SnO}$ is tetragonal, of the PbO type with $a_0 = 3.78 \text{ \AA}$ and $c_0 = 4.79 \text{ \AA}$.
3. The precipitate formed by the interaction of solutions of a stannous salt and NH_4OH has been found by a temperature-composition isobar and x-ray diffraction studies to be the hemihydrate, $2\text{SnO} \cdot \text{H}_2\text{O}$.
4. Stannous oxide hemihydrate is dehydrated into $\alpha\text{-SnO}$ by (a) the action of excess alkali, (b) the action of light especially in the absence of free ammonia, and (c) heating to temperatures above 120° and below 550° .

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THE SORPTION OF VAPORS ON WOOD AND CELLULOSE

BY N. H. GRACE* AND O. MAASS

The following study of vapor sorptions by cellulose and cellulose materials** makes use of a quartz spring balance suspended in an evacuated glass system. Advantages are claimed for the special technique employed. The results of water vapor sorption on various species of woods are given and compared with the sorption on cotton cellulose. The main feature of this paper, however, deals with the sorption of hydrogen chloride on cellulosic materials in the presence of previously absorbed water, because of the information this gives regarding the mechanism of sorption on such materials. The sorption of a number of other vapors is tabulated.

The sorption of water vapor on cotton has been studied extensively in the Shirley Institute and in the Eastman Kodak Laboratories under the direction of Dr. Sheppard, their results are recognised by the authors as fundamental. Hence, allusions to determinations made with cotton may be taken as being for purposes of comparison. However, certain advantages are claimed for the experimental method described by the authors, which is unique (in this sense) that where adsorption or desorption values are determined, these are carried out at a constant vapor pressure in the case of water vapor. Furthermore, the small amount of sample which can be examined gives results which are believed to be more nearly absolute, and therefore more comparable with determinations of Sheppard and Newsome¹ who use the quartz spring balance although they do not use the same experimental procedure of maintaining constant vapor pressure. A comparison, however, of the results obtained by various experimenters and an explanation of differences obtained, is to be left to another paper which will be published shortly.

As in the case of the investigations carried out by Pidgeon and Maass,² this paper must be considered as striving to deal with data in a new field, that of the sorption of vapors on wood and of using sorption values on other cellulosic materials for purposes of comparison, in order to obtain information on the properties of cellulose as it exists in wood.

The term sorption is used to indicate the amount of sorbed substance on the basis of percentage composition of the system. The term absorption is used to indicate the amount of sorbed substance on the basis of percentage composition of the system when the system previous to the determination contained a considerably smaller amount of sorbed vapor. The term desorp-

* The work described was carried out under the tenure of two scholarships granted by the National Research Council of Canada.

** This research was carried out in the Institute of the Pulp & Paper Association as a part of "Penetration Studies" under the direction of Dr. Maass. It was also included in the research programme of the Forest Products Laboratory at Montreal.

¹ J. Phys. Chem., 33, 1817 (1929).

² J. Am. Chem. Soc., 52, 1053 (1930).

tion is used to indicate the amount of sorbed substance on the basis of percentage composition when the system previous to the determination contained a considerably larger amount of sorbed vapor. In the desorption values given for water vapor on wood the reader is referred to the article quoted in which the determinations are described in detail.

Experimental

Fig. 1 indicates the essential features of the system in which sorption occurs. Actually, several different units have been employed in this investigation. These were modified to meet the particular requirements of special cases; there has, however, been no important variation in principle.

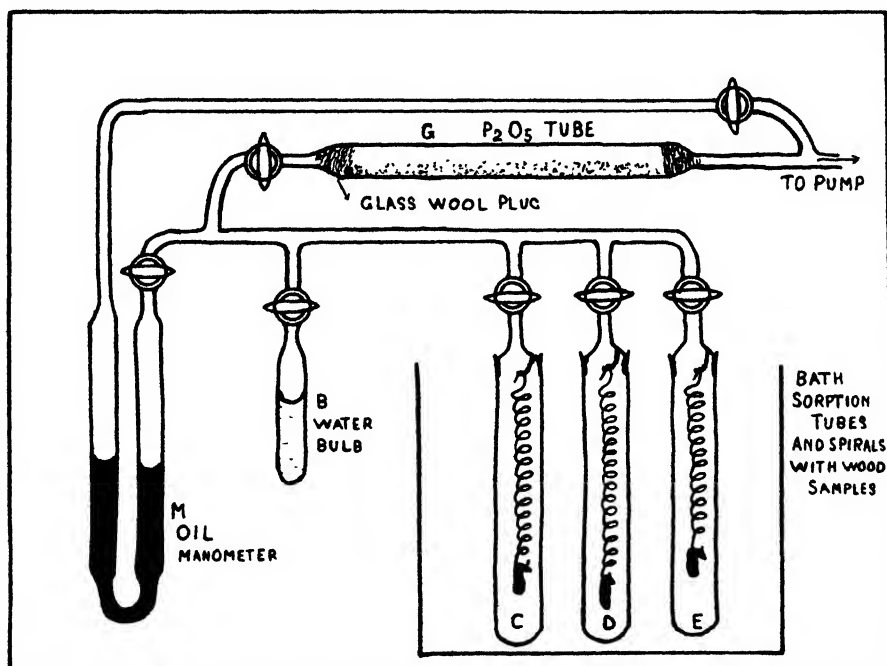


FIG 1

The glass tubes *C*, *D*, and *E*, are removable, the-ground glass joints are indicated in the diagram. The tubes are about eleven inches in length, with an inside diameter of one inch. A small glass hook, sealed into the glass head, serves as a support for the quartz spring balance. These tubes have functioned in a satisfactory manner as containers for spiral and sample. No tendency to leak at the large ground-glass joint has been observed. In the case of the tubes most recently placed in service any possibility of leakage has been eliminated by the presence of a flange on the tube, this may be filled with mercury. Another improvement, not indicated in the diagram, is a change in the position of the connecting tube. By inserting this in the side

of the large tube the ground-glass top may be removed without removal of the thermostating bath. The diagram indicates three sorption chambers in series. In practice it has been found convenient to use as many as 6 of these together. This system was confined to a study of the water vapor equilibria of woods and cottons.

The tube *B* contains water and serves as a source for vapor. It is surrounded by a Dewar flask maintained at a constant temperature, and thus the vapor pressure may be controlled.

The oil manometer is shown *M*. The oil used is "Cenco Hyvac" pump oil, and has a density about $1/15$ that of mercury, and also a negligible vapor pressure. This enables ready and accurate observation of the vapor pressures of water in the system. Where gases are used which require the measurement of greater pressures than can be indicated by this oil manometer, or with which chemical action may occur, substitution is made for the oil manometer *M*, of a mercury manometer. This is capable of indicating pressures up to 80 cms. of mercury.

The position of a phosphorus pentoxide tube *G* is indicated in the diagram, it is used in the determination of the dry weight of the sample. Further, the tube takes up water very readily, thus avoiding the actuation of the pumping system for the removal of small amounts of water vapor.

The bath surrounding the sorption tubes is indicated by the heavy lines. The bath in use consists of a container with a flat plate glass surface. An aquarium, of suitable size to accommodate a battery of 6 sorption tubes, has been found quite satisfactory. The bath is equipped with a stirrer which ensures rapid and thorough circulation. The heating element is controlled by a toluene mercury thermo-regulator through a relay. This regulates the temperature in a satisfactory manner, the maximum fluctuations being in the neighborhood of 0.02°C . Further, a cooling coil of lead piping through which a variable stream of cold water circulates, permits the use of temperatures which are below those of the room, thus increasing the temperature range over which investigation may be conducted.

The pumping system consists of a Langmuir mercury condensation pump backed by a Hyvac. The gas pressure in the system is determined by means of a MacLeod gauge which is capable of indicating pressures down to 0.0005 mm of mercury. In all experiments the pressure is first lowered to at least 0.001 mm before a run is commenced.

Observation of the extensions of the quartz spring balance is made by a cathetometer. The instrument used is capable of giving readings accurate to 0.02 mm. Spirals were constructed from quartz after the method of McBain and Bakr.³ The spiral is calibrated throughout the working range by observing the deflections caused by known weights. On the average a deflection of 1 mm corresponds to a weight of 0.0030 g. Thus, with the particular cathetometer employed, a weight of 0.0001 g can be easily detected, and the total weight of a sample weighing 0.1 g can be determined accurately to within 0.1% .

³ J. Am. Chem. Soc., **48**, 690 (1926).

Since the maximum differences observed are not greater than 30% of the total weight, the theoretical accuracy is well within 0.5% of the differences noted.

The sample is dried by long evacuation in the presence of phosphorus pentoxide at a pressure of about 0.0005 mm mercury. After approximately 12 hours a constant weight is observed. This weight is arbitrarily considered as the "dry weight," and the percentage increase due to sorption is always calculated on this basis. This point is completely reproducible, and may be checked several times, even after the sorption of water vapor. However, this reproducibility is not always found when other gases are used. It only holds when the sorbing system suffers no permanent change.

The Sorption of Water Vapor

The details of experiment and the results of water vapor sorption by cellulose and woods will be found in the Canadian Journal of Research. The following will merely touch on the most important conclusions of this work.

An attempt was made to correlate the "variation in the sorption" of the various woods with some of their other physical properties, such as density and hardness, but without success. The most important generalization to be found, is the great similarity in the amount of sorption for all the woods, twenty in number, examined to date. The desorption isotherm was found to be the least variable property of the woods examined, its variation from wood to wood being small.

It is of interest to note that of the 20 woods examined, in 11 the heartwood has the greater sorption, in 6 they are approximately the same, and in only 3 is there distinctly greater sorption in the sapwood. This means that, as a rule the heartwood has a greater sorption than the sapwood. Below is given a table which contains average sorption values. From this it will be seen that

TABLE I

Average Desorption Values for Woods and Cottons—% Sorption

Relative Humidity %	17.3	51.8	86.4
Vapor Press. mm, Hg.	3	9	15

Average Values for Twenty Species of Wood

Sapwood	4.90	10.50	19
Heartwood	5.20	11.10	20.4
Average	5.05	10.80	19.70

Values for Extracted White Spruce

Sapwood	5.25	10.70	21.25
Heartwood	5.00	10.10	19.10
Average	5.10	10.40	20.20

Values for Cotton Cellulose

Cotton (1).	2.80	5.70	12.15
Cotton (2).	3.30	6.85	13.30

the heartwood has a somewhat greater sorption than the sapwood on the average.

The values obtained for extracted wood are for two samples which gave practically identical values. The extraction was carried out in a standard manner, refluxing for several days in 1% sodium hydroxide in an atmosphere of nitrogen.

The desorption values for cotton (1) were determined on a rag cotton obtained from Eastman Kodak Co., and which had been subjected to careful purification. The values for cotton (2) are the desorption values obtained by Urquhart and Williams.⁴

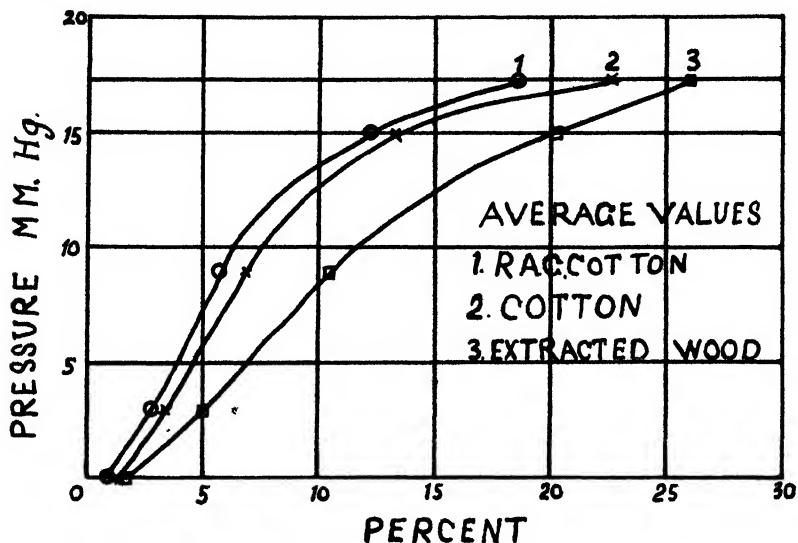


FIG. 2
Sorption of Water Vapor

Figs. 2 and 3 give a graphical representation including the data listed above. It is clearly shown that the extraction, which has removed all the carbohydrates, resins etc. and left only the cellulose and most of the lignin, has reduced the sorption by only very little. This reduction is, for the most part, in the region of high relative humidity, where the gross structure of the material plays a part.

It follows definitely, that the experiments of Pidgeon and Maass² have been corroborated as far as these showed that the sorption of water vapor by wood is on a much greater scale than the sorption by cotton. This is true over the whole range of vapor pressures, both for the wood in its natural state, and for the extracted samples.

The discussion of sorption values at 100% relative humidity and at 0% humidity is left to another paper, although these are shown in the graphs. Sufficient to say here that these are extrapolated values and not to be compared with experimentally determined ones.

⁴ Shirley Institute Memoirs, 3, 197 (1924).

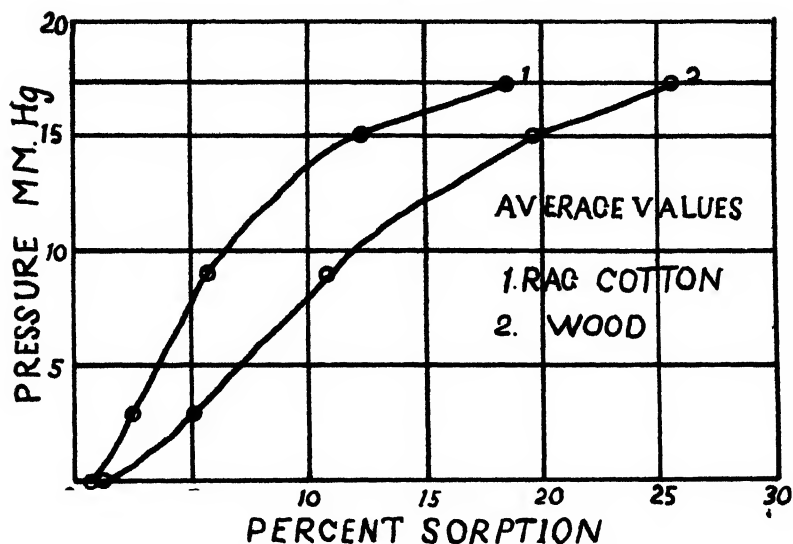


FIG 3
Sorption of Water Vapor

The Sorption of Hydrogen Chloride by Wood and Cellulose

When cellulose is brought into an aqueous solution of hydrogen chloride it hydrolyzes, the cotton undergoes a marked change in physical properties. No measurements of the sorption of hydrogen chloride gas in cotton and wood, as far as the authors know, have been carried out. In view of the change mentioned above, such an investigation is of interest.

It should, perhaps, be mentioned that most carefully prepared anhydrous hydrogen chloride was used. The gas was bubbled through 2 wash bottles of concentrated sulphuric acid, and finally over 2 phosphorus pentoxide tubes. This ensured a perfectly dry sample of gas coming into contact with the wood and cotton under investigation.

The first experiments attempted were with a dry cotton, and it soon became apparent that equilibrium was only brought about after a very long time. Below are the sorption values that were obtained. From the flattening out of the time curve they are supposedly equilibrium values, each is the result of a 90 hours experiment. It is seen that quite appreciable amounts of HCl are absorbed.

Sorption of Hydrogen Chloride by Cotton Cellulose.

Equilibrium value at 5.40 cm press. of gas 0.80%.

Equilibrium value at 70.20 cm press. of gas 2.00%.

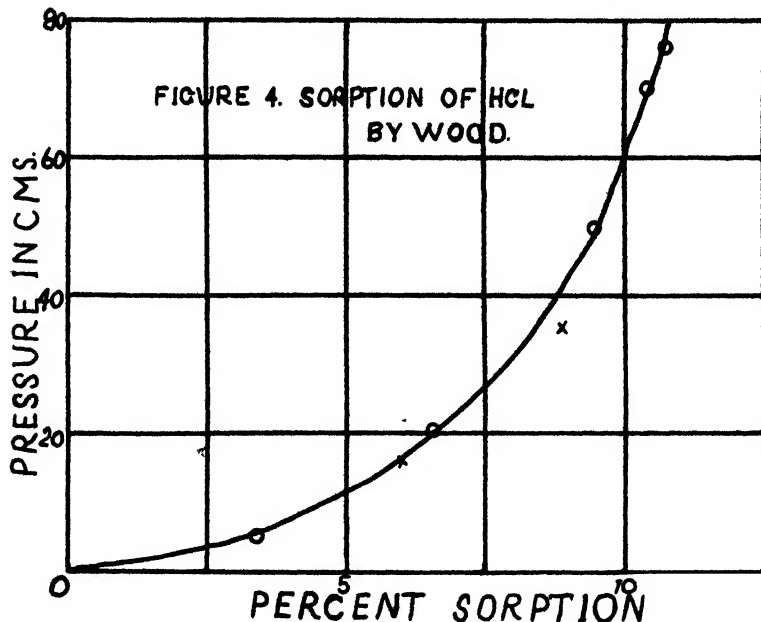
Sorption against Time

Time (hours)	% Sorption	Time (hours)	% Sorption
17	1.26	70	1.90
28	1.49	87	1.95
52	1.61	94	1.95
64	1.83		

(Final gas pressure 70.20 cm. Temperature 22°C)

On applying the vacuum, the HCl came off fairly readily until 0.80% was left. There had been little change in the appearance of the sample. Only at the higher HCl pressure did it take on a greyish tinge. On heating in vacuo, at 50°C the last trace of HCl was driven off, and the original weight of the sample was reached. It was judged that the HCl was absorbed by the cotton and could be desorbed, but the time required for equilibrium to be reached, made it impractical to carry out a detailed sorption isotherm.

When the cotton was replaced by a sample of white spruce heartwood, it was found that equilibrium was established much more rapidly, only one third



of the time being required. The equilibrium values for sorption are given below, and also the data for a typical time curve. Column 1 indicates that 2 samples were used, and the sorptions obtained (col. 2) at various pressures of HCl (col. 3) are shown in Fig. 4 to lie on a smooth curve. To test out desorption sample 1, after having been maintained at a pressure of 76.90 cm was kept until equilibrium resulted at a pressure of 35.40 cm. This gave a desorption value of 8.07%, which it is seen, lies fairly well on the absorption isotherm, indicating that there is little or no hysteresis. This, of course, will have to be confirmed when time permits. In a vacuum the absorbed HCl was taken out fairly rapidly until a residue of 2.24% was reached after 24 hours.

The form of the isothermal sorption curve is apparently quite different from the sorption curve with water vapor, and approaches more nearly to the form of a Freundlich adsorption. It is true that in terms of relative vapor pressure—as far as HCl is concerned—it is only a small fraction of the saturation value that has been examined. But the criterion for similarity is found in the sharp upturn of the curve. Before discussing this phase any further it is

Sorption of Hydrogen Chloride by White Spruce.

Sample	% Sorption	Pressure (cm Hg)	Sample	% Sorption	Pressure (cm Hg)
1	3.38	5.50	2	10.71	76.90
1	7.60	20.09	Desorption Equilibrium Values		
2	9.40	49.60	1	8.97	35.40
1	10.37	70.60	2	7.01	16.00

(Temperature 22°C)

Sorption against Time

Time (Hours)	% Sorption	Time (Hours)	% Sorption
$\frac{1}{2}$	2.54	10	6.02
2	4.08	21	6.72
3	4.43	24	6.93
4	5.23	27	7.32
$5\frac{1}{8}$	5.53	31	7.42
$7\frac{3}{8}$	5.83		

(Final pressure 20.09 cm. Temperature 22°C)

Desorption of Hydrogen Chloride against Time.

(Initial value 10.71% HCl)

Time (Hours)	% Sorption	Time (Hours)	% Sorption
$\frac{1}{4}$	8.57	$3\frac{1}{4}$	4.83
$\frac{1}{2}$	7.67	7	3.13
1	6.82	13	2.74
$1\frac{3}{4}$	5.63	$23\frac{1}{2}$	2.24

worth considering the experiments carried out with wood samples containing a definite amount of water, because in these cases, also, sorption curves were obtained similar in character to that of hydrogen chloride in dry wood.

The experimental procedure consisted in suspending a sample from the spiral and first of all bringing it down to dry weight. Then water vapor was brought into contact, until a desired amount of sorption had taken place. The stopcock, leading to the water bulb, was then closed, and HCl admitted to the desired vapor pressure. The latter was always many times that of the residual water vapor remaining in the apparatus, so that further absorption of water vapor could be neglected in comparison to the striking increase in sorption, which is to be discussed. A calculation shows that the maximum possible error due to all residual water being absorbed is in the order of $1/2\%$ of the dry weight of wood, and it is very unlikely that this would be reached. The direction in which error would take place would be, of course, to give an added apparent sorption of HCl. As a matter of fact, the addition of HCl will sweep any residual water vapor on to the walls of the containing vessel. This was made apparent in the case of highest water vapor pressure by the formation of a very fine mist. The experimental results follow.

TABLE II

Sorption of HCl by White Spruce containing absorbed water

% HCl	% HCl (held by H ₂ O)	% HCl (in wood)	V.P. (cm Hg)
(Amount of water absorbed by the wood . . . 1.67%)			
5.38	0.86	4.52	11.60
8.83	1.04	7.79	40.60
11.22	1.16	10.06	74.70
(Amount of water absorbed by the wood . . . 3.29%)			
5.24	1.64	3.60	5.30
6.97	1.73	5.24	11.00
8.40	1.82	6.58	21.30
10.26	2.19	8.07	40.70
11.24	2.37	8.87	76.00
(Amount of water absorbed by the wood . . . 5.05%)			
10.50	2.49	8.01	11.70
13.08	3.04	10.04	41.00
14.22	3.36	10.86	73.00
(Amount of water absorbed by the wood . . . 7.46%)			
11.55	3.82	7.73	9.70
15.63	4.70	10.93	41.00
17.17	5.22	11.95	74.30
(Amount of water absorbed by the wood . . . 9.47%)			
15.74	5.16	10.58	11.50
19.74	6.13	13.61	43.70
22.46	6.84	15.62	73.80
(Amount of water absorbed by the wood . . 12.30%)			
18.45	6.27	12.18	9.50
24.28	7.74	16.54	41.20
27.04	8.61	18.43	72.40

The first column in the above table indicates the amount of HCl taken up by the system wood-water. The second column indicates the amount of HCl calculated as dissolved in the water present, on the assumption that the water is unaltered. (The calculation is made from data found in Landolt-Börnstein, page 1397). The third column represents the actual sorption by the wood. It is obtained by subtracting the amount of HCl, calculated as existing in solution in the absorbed water, from the total amount of sorbed HCl. The fourth column indicates the HCl pressure at which the equilibrium point was determined.

It is of interest to note that the equilibrium sorption values were reached more rapidly with wet wood than is the case with dry wood. The difference is most striking with wet and dry cotton. Whereas 90 hours were required with the dry cotton (the data have already been given), 3 hours sufficed when water was present. The data for a typical case follow.

The Sorption of HCl by Cotton with Absorbed Water.

Sorption against Time

(Amount of water absorbed by the cotton . . . 2.92%)

Time (hours)	% HCl Sorbed	Time (hours)	% HCl Sorbed
$\frac{1}{4}$	2.91	$1\frac{1}{2}$	4.15
$\frac{1}{2}$	3.39	2	4.24
1	3.86	3	4.33

(Final gas pressure was 10.40 cm Hg)

On raising the pressure of HCl to 41.50 cm Hg the following gives the sorption.

Time (hours)	% HCl Sorbed	Time (hours)	% HCl Sorbed
1	5.46	6	5.93
2	5.65	8	5.90

In the case of the wet wood samples evacuation brought the weight down to within 2% of the dry weight. After heating to 50°C a semi-permanent increase of 1% was still observed. In the case of cotton, heating reduced the residual increase of 4.6% to an actual loss of 1.3% showing that some permanent change has taken place. However, a water sorption isotherm on such a sample showed very little change, except at the initial stage, where there was a decreased absorption. If the comparison is made with the initial sorption, of a specially purified cotton, this is not so great. (The comparative data follow.) In the case of wood, only the first part of the water sorption isotherm was examined, and this, as with the cotton, showed a small decrease in the water absorption of the hydrogen chloride treated wood.

The Sorption of HCl by Cotton containing Absorbed Water.

% HCl	% HCl (In water)	% HCl (By cellulose)	V.P. (cm Hg)
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(Amount of water absorbed by the cotton . . . 2.92%)

4.42	1.45	2.97	10.40
5.93	1.86	4.07	41.50
6.49	2.04	4.45	74.50

(Amount of water absorbed by the cotton . . . 4.32%)

6.90	2.20	4.70	9.90
9.20	2.72	6.48	41.60
9.93	3.02	6.91	75.20

The Water Sorption of HCl-treated Moist Cotton as contrasted to that which is untreated.

% Sorption		Relative V.P. (%)	% Sorption		Relative V.P. (%)
Untreated	Treated		Untreated	Treated	
1.00	0.60	10	5.55	5.40	60
1.60	1.20	20	6.35	6.60	70
2.40	2.25	30	7.40	8.00	80
3.40	3.30	40	8.45	10.00	90
4.35	4.30	50	11.00	12.80	100
					(extrap)

By means of the data contained in the preceding pages, a composite table can be formed, giving interesting information. This is given below.

TABLE III
The Sorption of HCl by White Spruce Heartwood

% Sorption							V.P. (cm Hg)
0%	1.67%	3.29%	5.05%	7.46%	9.47%	12.30%	
3.20	3.20	3.35	6.40	7.00	9.30	11.15	5
5.70	4.25	4.90	7.67	7.85	10.20	12.20	10
7.40	5.60	6.52	8.87	9.15	11.50	13.95	20
8.27	6.80	7.50	9.45	10.00	12.55	15.30	30
8.90	7.72	8.05	9.98	10.70	13.35	16.35	40
9.35	8.55	8.37	10.37	11.20	14.05	17.20	50
9.86	9.25	8.60	10.62	11.55	14.75	17.90	60
10.36	9.90	8.79	10.80	11.70	15.40	18.35	70
10.54	10.10	8.87	10.87	11.90	15.80	18.50	75

This table is made up of values read off curves plotted for each of the runs which have just been given. Each column is headed by the percentage of water present. Since the first column gives values for the sorption of HCl by dry wood, and since all the other values have been corrected for the acid held by the water, reading across in a horizontal manner one observes a range of HCl sorptions at one gas pressure, but by samples with different amounts of absorbed water.

These results can be interpreted in a number of ways, and it is rather difficult to decide which is the correct interpretation. Suppose, first of all, one considers the water absorbed by the wood to be unchanged in its power to dissolve HCl. Then the values in the table, which were calculated on this basis, show that in samples having less than 4% of absorbed water, the wood sorbs less HCl, while above 4% it sorbs more HCl, than the dry sample. On the other hand one might assume that the sorption of HCl, on wood is unaltered, and that the absorbed water has changed in relation to its capability of dissolving HCl. This would mean that the water absorbed in samples con-

taining the highest percentages of water, dissolved HCl better than ordinary water. The water absorbed to high percentages is, however, more likely to retain its usual characteristics than the first water that is absorbed. Doubtless the first 1 or 2% of water absorbed by wood will not have the same solvent action on the HCl as ordinary water, but with increased water content the ordinary water properties should be approached more and more by the absorbed water.

Recent work by Filby and Maass* on the density of water sorbed by cellulose is of interest in this connection. The variation in hydrogen chloride sorption for wood containing about 4% sorbed water has its counterpart in the density change observed in this same region for water sorption by cotton cellulose. It has been shown that the first few % of water sorbed by cellulose has a density of 2.4. This high density is constant at first and then falls with further sorption until it becomes asymptotic to the value 1. This would indicate a very intimate relationship existing between the first few % of sorbed water and the sorbing material.

It is not surprising, in the light of this density change, that the first few % of sorbed water form a system which absorbs less hydrogen chloride than the two components alone. The subsequent addition of water beyond 4% results in greatly increased surface due to swelling action. This will be amplified below.

Some experiments carried out on HCl sorption by samples containing water left after desorption had taken place, are interesting in connection with what was said above. Two samples were first of all saturated with water vapor, then desorption was allowed to take place until a value was reached, as near as possible to an absorption value. The experimental data are given below. Following this a table is given in which 5.40% desorption is compared with a 5.05% absorption, and a 7.88% water desorption value is compared with an absorption one of 7.46%.

The Sorption of HCl by Wood containing Desorbed Water Vapor.

% HCl	% HCl (Held by water)	% HCl (By wood)	V.P. (cm Hg)
(Amount of desorbed water 7.88%)			
9.85	4.01	5.84	9.30
14.17	4.99	9.18	42.60
16.08	5.50	10.58	74.13
(Amount of desorbed water 5.40%)			
8.16	2.74	5.42	9.40
12.33	3.34	9.01	39.10
14.21	3.76	10.45	71.00

* Can. J. Research, 7, 162 (1932).

TABLE IV

Sorption of HCl by White Spruce Heartwood following Adsorption and Desorption of Water Vapor

% Sorption				V.P. (Cm Hg)
5.05% (Abs)	5.40% (Des)	7.46% (Abs)	7.88% (Des)	
6.40	4.30	7.00	5.35	5
7.67	5.35	7.85	6.00	10
8.87	7.00	9.15	7.15	20
9.45	8.15	10.00	8.20	30
9.98	9.00	10.70	8.95	40
10.37	9.60	11.20	9.60	50
10.62	10.10	11.55	10.10	60
10.80	10.45	11.70	10.50	70
10.87	10.60	11.90	10.60	75

Each column is headed by the percentage of sorbed water.

From the results of Table III the amount of HCl sorbed increases with the amount of water present, above the 4% sample. Thus, if the fact of the equilibrium water value being absorption or desorption is of no consequence, one would naturally expect the two "desorption" woods to take up the largest amount of HCl, as each exceeds the "absorption" value by about 0.40%. However, both woods with the larger amount of water—but present as equilibrium desorption values—sorb decidedly less HCl than the woods with less water—but water present through absorption. Apparently the wood has a lessened ability to take up acid when the water exists there following absorption.

In the above table (Table IV) is given the percentage sorbed on the dry wood, that is, after the HCl dissolved in the water has been subtracted, as was described before. Before discussing the reason for this, it is necessary to see whether any information can be obtained with regard to the nature of the HCl sorption.

As was pointed out before, the absorption curve for HCl has a different form from that of the water sorption isotherm. If both of these are tested by applying Langmuir's adsorption formula

$$x/m = abp/(1+ap).$$

it is found that the water sorption does not follow this, whereas the HCl sorption of both dry and wet wood does, it also holds for HCl sorption by wet cellulose. In Fig. 5 curve 1 represents the sorption of water in cellulose, and 2 that of HCl by wet cotton cellulose. According to McBain⁵ the interpretation that is given is that in the case of HCl we are dealing with a straight surface adsorption, whereas in the case of water, part, at least, must be due to filling up of the interstices between the actual cellulose and part to adsorption. If the HCl sorption is surface adsorption, then the interpretation that can be

⁵ J. Am. Chem. Soc., 52, 2668 (1930).

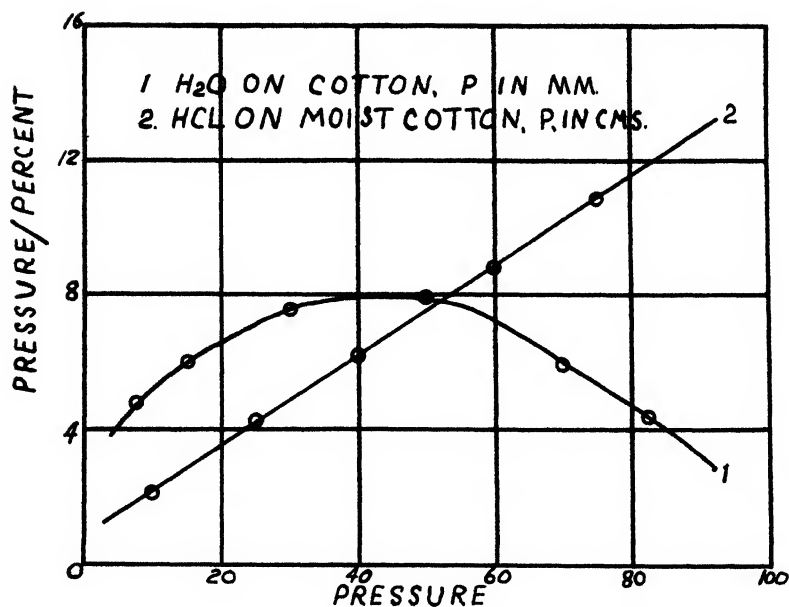
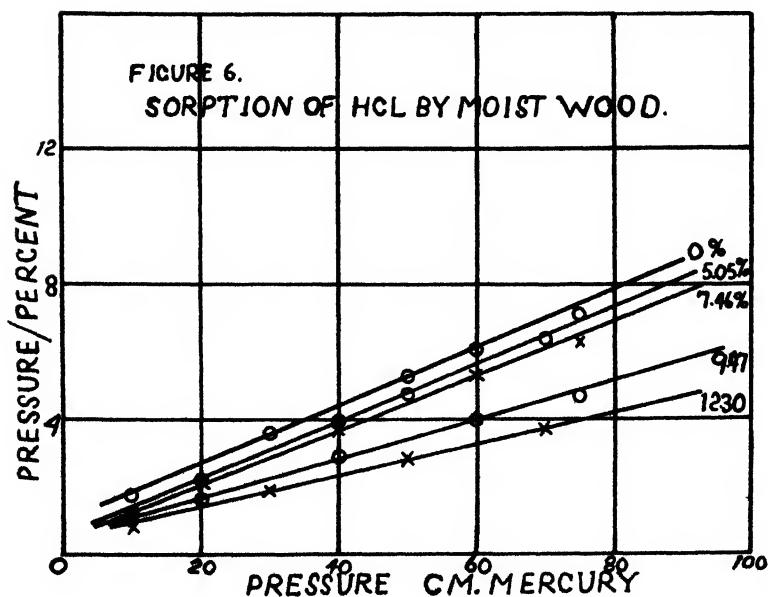


FIG. 5



put to increased sorption of the wet samples (above 4% moisture content) is that the water increases the active surface of the cellulose, on which adsorption takes place. In that case the application of Langmuir's formula to the data of Table III should also give straight lines. Fig. 6 shows that this is the case. On each curve is indicated the percent of water. The only one not conforming to a straight line is the one just below 4% of sorbed water. The decrease in HCl sorption below 4% water content, can then be explained by the active surface being partially used up by the absorbed water. This effect will, of course, hold for all the other determinations, but is more than counter-balanced by the increase in active surface, caused by the addition of the larger amounts of water.

The decrease in sorption, when water is left by desorption, can also be explained. The water, so held, is more intimately associated with the cellulose, as is shown by the lower vapor pressure of the water desorption point. This results in a greater decrease of the active sorbing surface available for the HCl sorption.

The Sorption of Sulphur Dioxide, Ammonia and Carbon Dioxide by Wood and Cellulose

Cotton cellulose takes up sulphur dioxide exceedingly slowly, over 100 hours is required for the establishment of equilibrium. At a gas pressure of 76 cm and at 22°C approximately 5% is sorbed. The last 0.80% of this is held very rigidly, ordinary evacuation does not, over a period of 3 days, remove this part of the sorbed gas. However, 3 hours of heating at 85°C removed the last traces.

The sorption of sulphur dioxide evidently does effect some permanent alteration in the cellulose. The sorption values indicated above are not reproducible. The second sorption at an identical gas pressure gives a sorption value of 3.09% as compared to 5.10% initially determined. Further, a water vapor sorption was determined on this sample, and there results a slight change in sorption capacity, in the region of high relative humidities. There is an increase in sorptive power comparable to that found in the case of hydrogen chloride treated cellulose.

A characteristically different behavior is noted when wood is considered. Spruce sapwood alone has been investigated.

There is a much larger amount of sulphur dioxide taken up by the wood, than is the case with cotton, 13.6% as compared to 5%. Further, the time to reach the true equilibrium condition is comparatively small, 10 hours is the time interval at 76 cm pressure of the gas. Another marked difference is the much greater amount of the residual gas. After 24 hours evacuation nearly 4% of the sorbed sulphur dioxide is still held by the wood. This is, however, readily removed on heating to 85°C.

In general the results with ammonia are similar to those which have just been discussed. Approximately 4% of ammonia is sorbed by cotton cellulose at 76 cm pressure. Equilibrium takes roughly 48 hours. However, the sorbed gas is very easily removed, one hour on the vacuum effects its complete elimination.

As was the case with sulphur dioxide and wood, the latter takes up much more ammonia than does cotton. The equilibrium value is reached in about 12 hours, and indicates a sorption of 7.37% at 76 cm pressure of ammonia. All but the last 1% of the sorbed ammonia is quite easily removed on evacuation. However, even heating to 95°C still left a residue of 0.40%.

The work to date with sulphur dioxide and ammonia is merely introductory. However, even from such preliminary experiments, certain generalizations seem to be justified. With wood the attainment of equilibrium takes much less time than with pure cotton cellulose. The modifying influence of the non-cellulose constituents, as well perhaps, as its structure, evidently influence the sorbing system to a marked extent. Also the degree of sorption is quite different with the wood samples investigated. It is on a much larger scale.

Carbon dioxide is not appreciably sorbed by cellulose, up to a gas pressure of 76 cm. Further, if the cotton cellulose contains 5% of absorbed water there is still absolutely no sorption evident. With wood, 1.07% of sorption takes place at a pressure of 42 cm. Raising the pressure to 76 cm causes no increase in the amount of sorption. The sorbed gas is readily removed. Starting with 0 sorption and a pressure of 76 cm only 1.03% of carbon dioxide is sorbed. From 0 sorption and at 22 cm pressure, a sorption of 0.75% is observed. Apparently sorption becomes asymptotic to the value 1% somewhere between a gas pressure of 22 cm and 42 cm. If wood contains 3.36% of water, there is absolutely no sorption of carbon dioxide by such a sample. The water completely inhibits the appreciable retention of carbon dioxide.

The Sorption of Ethyl Ether, Amylene and Methyl Alcohol by White Spruce Heartwood

The investigation conducted with the above vapors has been merely introductory. However, it is felt that the results are of interest, and also, that further profitable lines of study may be indicated.

Sorption of Ethyl Ether.

The sorption took place at 22°C.

Equilibrium was reached, on the average, in about 12 hours.

% Sorption	Vapor Pressure (cm Hg)
0.53	10.20
0.69	19.60
1.16	38.20

The sorbed gas is readily and completely removed on evacuation.

These results indicate that there is very slight tendency for wood (white spruce heartwood) to take up ether, even when the relative vapor pressure approaches 90%. No work has been done on the sorption of this vapor by cotton cellulose. However, it is to be expected that the extent of sorption would be very slight as in the case of all the other vapors investigated to date, wood takes up considerably more than does cotton cellulose.

Sorption of Amylene.

At 10 cm pressure no appreciable sorption occurs, on raising the pressure to 25 cm a sorption of 0.47% is observed. Further increase of the vapor pressure until condensation took place (100% relative vapor pressure) resulted in an unchanged sorption. Thus, this unsaturated hydrocarbon is taken up to an even smaller extent than is ethyl ether.

The Sorption of Methyl Alcohol.

% Sorption	Time (minutes)	% Sorption	Time (minutes)
2.19	10	4.66	60
2.69	15	4.92	75
3.23	20	5.22	105
3.58	25	6.12	270
3.91	35	6.42	16 (hours)
4.10	45	6.42	18 "

(Final pressure 3.70 cm. Temperature 22°C)

Equilibrium Sorption Values

% Sorption	% Relative Vapor Pressure	% Sorption	% Relative Vapor Pressure
6.42	34.41	8.21	60.34
7.19	54.31	11.69	83.15

Equilibrium Desorption Values

10.05	50	8.37	31
9.54	44	7.61	27

These results indicate quite clearly that the sorption of methyl alcohol by wood takes place on a relatively large scale. Also the fact of definite and marked hysteresis is very evident. Time has not permitted a detailed study of this system but the indications are that this will eventually prove to be an extremely interesting field, especially when comparisons are made with similar data to be obtained from cotton.

Discussion

As was indicated in the introduction, no revolutionary theories are to be drawn from the data which are presented above. However, in conclusion, a certain number of experimental facts are to be tabulated, followed by a working hypothesis whose main virtue may be looked on from the point of view of indicating the direction for further research.

Undoubtedly wood sorbs water vapor to a greater extent than cotton cellulose, and since Pidgeon and Maass have shown that this increase in sorption is not due to the lignin and as the experiments on extracted wood have shown this is not due to the extractible portion of the wood, it follows that the cellulose in the wood sorbs water to a greater extent than cotton cellulose and perhaps even to a greater extent than mercerized cotton. The sorption of water

vapor in wood seems to be independent in large measure of the species and to be of the same order of magnitude for sap and heartwood. The comparative sorption experiments of various vapors on wood and cotton indicate that wood in every case sorbs a larger amount of vapor, and also, that in every case the steady state sorption value is obtained far more readily in wood than it is obtained in cotton.

The authors believe that the hypothesis advanced by Pierce⁶ with regard to water vapor sorption is in the main correct. Water is sorbed in two ways; one involving a surface compound formation perhaps on the basis of one of water to one exposed hexose group, in the other the rest of the water is used to fill spaces available under attractive forces like those in a liquid. The volume change observed by Filby and Maass in the addition of the first bit of water is in agreement with the sorption of hydrogen chloride experiments described above. They indicate that this water loses its ordinary characteristics, and therefore, this water is to be regarded as directly combined. The experiments, however, seem to indicate that with increased sorption of water the surface available for such compound formation is also increased. Without regarding the following as a rigid way of presenting what happens, it is tentatively suggested that the cellulose micelles offer a certain free surface for this surface addition of water and that this surface is increased when actually liquid water fills the interstices at the edges of the micelles. At that point the competition of cellulose surface for cellulose surface goes into competition with that of cellulose surface for water. On this basis too the phenomenon of hysteresis is explainable. Originally, the cellulose surfaces being together, a certain amount of energy is required to displace them, before the water will take their place either partially or completely. Consequently, the amount of adsorption with continued increase in sorption of water vapor, lags behind a value which would be obtained were the micelle surfaces not acting upon one another. On desorption, that is with decreased concentration of water vapor, this hindrance has been removed, and the sorbed water has a greater value. It is tempting to go on to make further deductions, such as, that the cellulose in wood is in a much finer state of distribution, as far as the size of the micelles is concerned, corresponding somewhat to mercerized cotton. Such speculations, however, must be left until further work has been carried out.

The direction which further investigation should take is a comparison of sorption values of cellulose obtained from various sources. Especially, accurate determinations at the low relative humidity range are desirable. The heat liberated at various stages of water vapor sorption should be accurately measured. The experiments of Filby and Maass on water vapor sorption should be carried out with greater refinement over the whole sorption isotherm, both for adsorption and desorption. These researches are under way.

⁶ Shirley Institute Memoirs, 8, 35 (1929).

THE SORPTION OF SODIUM HYDROXIDE ON CELLULOSE AND WOOD

BY R. RICHARDSON* AND O. MAASS

This paper consists of data dealing with the effect of aqueous sodium hydroxide on cellulose, in particular with its sorption qualities. It is presented in the form of plates of some results obtained at the University of McGill.** In review, whereas cotton alkali sorption has been previously investigated, practically no results for wood cellulose are to be found in the literature. Wood cellulose was first used but it was natural to extend the measurements to other types of cellulose. In a practical way the related industries of mercerization, alkali cooking, and zanthating may make use of the results. Theoretically the subject is interesting from a standpoint of absorption in an abstract sense apart from the materials used. Since adsorption theory is in advance of absorption theory at presents experiments on absorption are particularly interesting.

The sorption calculations were made from measurements of the change in concentration of the liquid solution before and after contact with a known amount of the solid phase. For purposes of cursory investigation and of time factor determinations, conductometric measurements were satisfactory and flexible and were first used. For detailed work titrimetric and occasionally gravimetric methods were used. The samples for titration were secured in a weight pipette. The accuracy in analysis attained was such that the average deviation from the mean was 1 part in 4000 at 40% alkali. Each determination of a concentration consisted of the average of 3 such analyses. Quantities were adjusted to produce a concentration change of 0.5%. The samples of cotton and "Celanese" were purified by cooking in a one percent alkali solution for 4 days. The purification of spruce was attempted as can be seen from one of the spruce plates. Plate number 9. The lignin is partially attacked, however, and results are not repeatable. The sample denoted as "Celanese" has suffered considerable alteration in purification and is not to be compared with the original commercial sample. The acetyl number of the purified "Celanese" is being estimated to determine the degree of alteration but this value is not yet available. A reaction period of 1 hour was agreed on for celanese above 45% where the downward trend of the curve for "Celanese" is due to the slow diffusion in such viscous solutions.

There is a strong temptation to present nothing but facts and results since it is certain that with further investigation the interpretations given to certain

* Acknowledgment is hereby made of two scholarships granted to one of us by the Canadian Pulp and Paper Association.

** This work is part of a research program of "Penetration Studies" being carried out under the direction of Dr. Maass in the Institute of the Pulp and Paper Association. It is also part of the research program of the Forest Products Laboratories, Montreal.

of the curves must be changed. Such a course would be, however, dull. It is particularly requested that the deductions made at this time concerning the results be regarded as purely working hypotheses. Final conclusions cannot yet be hazarded.

The use of the terms sorption, adsorption, and absorption are familiar enough. In this article sorption is a general term. Adsorption refers to surface concentration on a solid structure. Absorption refers to internal concentration throughout the solid structure. The use of such terms as pseudo sorption and others is not so general. Anticipating criticism from their use they will be explained in some detail. It is obviously not expressing the facts to say that in a 25% solution of alkali 0.2 g of NaOH is sorbed per gram of cotton since there must be some water sorbed or associated with the cotton contemporaneously. The hygroscopicity of cotton suggests that cotton in solution would not be bone dry. There must be two values, one for alkali and one for water, for example, 0.3 g NaOH plus 0.3 g H₂O. Such true values have never yet been accurately obtained. The value 0.2 g NaOH is all that can be measured. It is a net result of the two true values. To express this fact it is perhaps permissible to use the term pseudo sorption to be applied to such a result as 0.2 g NaOH. It will be argued that the term is unnecessary since the true values have never been determined. In rebuttal it may be pointed out that the literature abounds with citations of molecular ratios of compounds calculated from pseudo sorption curves by investigators who have not realized that such values are only useful by comparison and are not absolute in nature. The use of such a term would caution against the misuse of sorption values. This case is not the only example of errors contracted by the promiscuous use of sorption values. Consider the addition of salt to the solution of alkali. Until the sorption of any of the three liquid constituents is proved equal to zero it must be assumed that there is a true value for each, one for alkali, one for salt, and one for water. By analysing for alkali alone and considering mathematically that the salt is water a value is obtained which is denoted as the uni-pseudo sorption value of the alkali. However, by analysing for all three components, the net difference between the true values of alkali and the actual water alone can be calculated. In this manner the bi-pseudo sorption of the alkali is obtained. The literature records only uni-pseudo values whereas bi-pseudo values are much better indicators of the true state of affairs.

The mathematical definitions of these sorption terms are given.

Symbols.

- a Bone dry weight of solid phase, gms.
- b Weight of solution used, gms.
- M Moisture content of the solid phase before the experiment, gms. H₂O per bone dry gm. of solid phase.
- x, y, z, the original concentrations of alkali, salt, and water in the solution, % by weight.
- x', y', z', the final concentrations of alkali, salt, and water in the solution, % by weight.

Case 1.

Let there be two liquid phase components, alkali and water, and it be desired to calculate the alkali as sorbed. Then the water is considered as unsorbed.

Pseudo sorption of x (alkali).

$$\frac{b(x-x')-x'aM}{a(100-x')} \text{ g/g solid phase.}$$

Case 2.

Let there be three liquid phase components, alkali, salt, and water, and it be desired to calculate the alkali as sorbed, and let the water plus salt be considered as unsorbed.

Uni-pseudo sorption of x (alkali).

$$\frac{b(x-x')-x'aM}{a(100-x')} \text{ g/g solid phase.}$$

The similarity of form to case one explains in part why these values were first used in place of bi-pseudo results. Note that y and y' need not be known.

Case 3.

Let there be three liquid phase components, alkali, salt, and water, and it be desired to calculate the alkali and salt as simultaneously sorbed. Then the water alone is considered as unsorbed.

Bi-pseudo sorption of x (alkali).

$$\frac{bxz'-bzx'-100aMx'}{100az'} \text{ g/g solid phase.}$$

Bi-pseudo sorption of y (salt).

$$\frac{byz'-bzy'-100aMy'}{100az'} \text{ g/g solid phase.}$$

Certain experimenters have erroneously considered M equal to zero. If M is small the error introduced is numerically small, as in the case of air-dry cotton. In other cases it cannot be ignored. The practice of neglecting M is likely to cause mistakes. Wood samples are usually presoaked in water so that equilibrium may be attained rapidly during the experiment and M in these cases is very large.

A factor due to the solution of the solid phase in the liquid phase is neglected in these formulae but is sometimes appreciable.

As a summary to these formulae and mathematical considerations it may be generalized that if there are n liquid phase components, having chosen one to be considered unsorbed (unless otherwise stated this is usually the solvent), $n-1$ simultaneous pseudo sorption values can be determined, one for each of the remaining liquid phase components. This is a much better procedure than choosing $n-1$ components to be unsorbed and calculating the sorption of the n th component, even if this operation be repeated until values for all components are obtained.

To illustrate these calculations and show that too much reliance must not be placed on uni-pseudo sorption values the boxed sorption values for sodium

hydroxide in Plate 1 may be compared. The addition of the salt has increased the sorption of alkali but the bi-pseudo sorption value shows that the increase is really not as large as would be concluded from the uni-pseudo value. The prefixes uni and bi refer to the number of liquid phase components which the mathematical procedure in each case permits having a simultaneous pseudo sorption value.

The above discussion shows that the results which will be given in the following tables can be relied on only to give the relative changes of sorption caused by a change in the concentration of the alkali or due to a different sample of cellulose. These results cannot be used in their present form and in the light of present knowledge to calculate stoichiometric proportions, etc. While it is sometimes possible to conclude that compounds are formed it is impossible to calculate their formulae.

In the authors' opinion no reliable and complete data for sorption of NaOH on cotton exists at concentrations above 30%. It was found that only when

PLATE 1

Spruce Flake Sorption

One hour, 20°C, in sodium hydroxide, salt, water systems

(A) Without salt.

Equilibrium solution % NaOH	Pseudo sorption g NaOH/bone dry g
4.562	0.0474
4.570	0.0353
4.348	0.0411
4.465	0.0397
4.508	0.0399
Average—	
4.591	0.0407

And by comparison with known adsorption values for another spruce sample:

3.9*

0.038

(B) With salt.

Equilibrium solution %NaOH—%NaCl		Uni-pseudo sorption g NaOH—g NaCl /bone dry g		Bi-pseudo sorption g NaOH—g NaCl /bone dry g	
3.837	9.705	0.0480	0.0382	0.0505	0.0428
3.899	9.625	0.0510	—0.0402	0.0498	—0.0337
3.850	9.625	0.0546	—0.0556	0.0528	—0.0504
3.898	9.713	0.0513	—0.0430	0.0497	—0.0346
3.920	9.148	0.0568	—0.0511	0.0551	—0.0471

Average of last four tests—

3.9*

9.5

0.053

—0.048

0.042

—0.042

* Comparable values.

experimental determinations of the highest accuracy were made that reproducible results were possible. At high concentrations equilibrium is attained very slowly and with great experimental difficulty. Below 30% the data in the literature was used. Plate 2 illustrates the cotton isotherm at room temperature. Rumbold's¹ very intensive examination at low concentrations has been linked by the work of Vieweg² to the present examination of high concentrations. The curve is generally interpreted as being a combined effect of solid solution (adsorption) and of compound formation, the latter

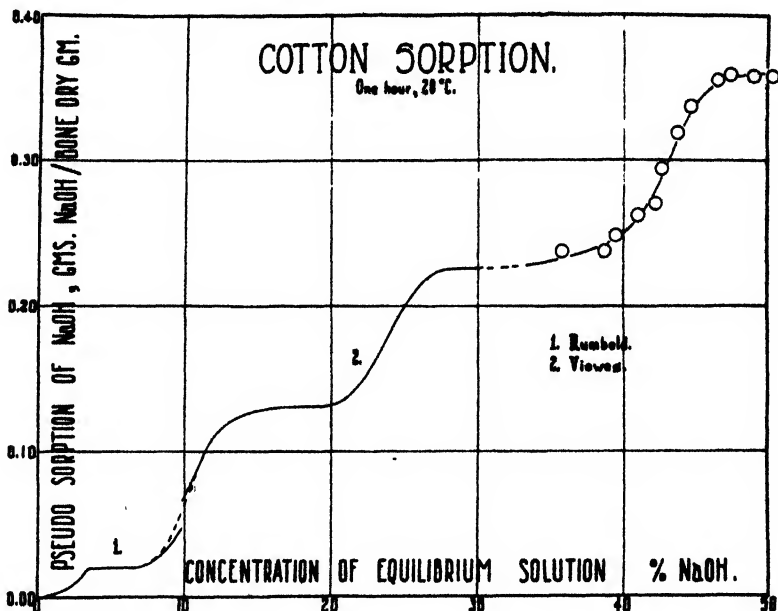


PLATE 2

Rumbold and Vieweg's values were not determined at one hour and 20°C but are nevertheless comparable with the determinations as shown by the circles; equilibrium in these cases being attained after very short time intervals.

indicated by the horizontal reaches. At low concentrations the cotton curve is in sharp contrast with the curves for wood and "Celanese." The latter curves obey Freundlich's adsorption law. If the cotton curve is considered to be concave then the wood and "Celanese" curves are convex below ten percent sodium hydroxide. The theory of the cotton curve is based on applications of the phase rule. Dalton's law of partial pressures may also be applied. In Nernst's Theoretical Chemistry it is cited as Dalton's law of absorption and as such applies to the absorption of gases in liquids. In this case it is extended to the distribution of alkali between the liquid solution (water) and the solid solution (cotton). Except for aberrations from the laws of ideal solutions a straight line relationship between sorption and concentration would indicate absorption. This rule for absorption takes the place of Freundlich's relation

¹ J. Am. Chem. Soc., 52, 1013 (1930).

² Ber., 40, 3876 (1907).

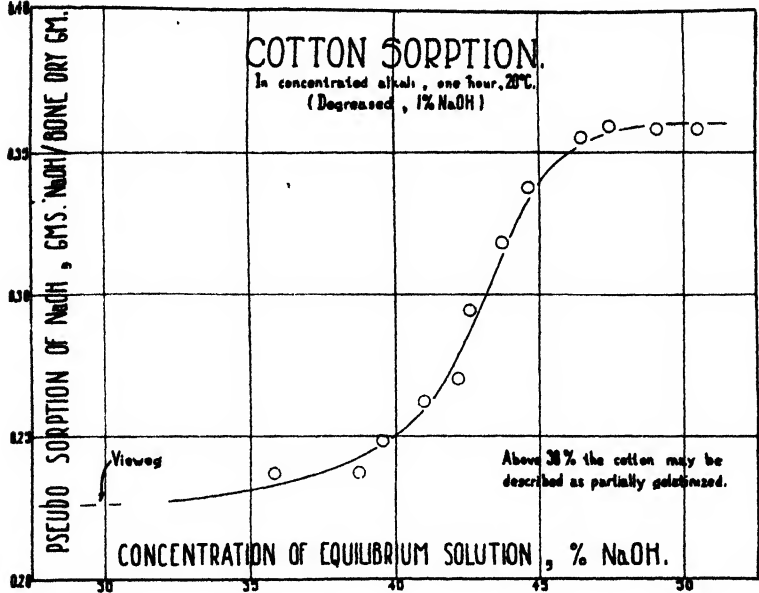


PLATE 3

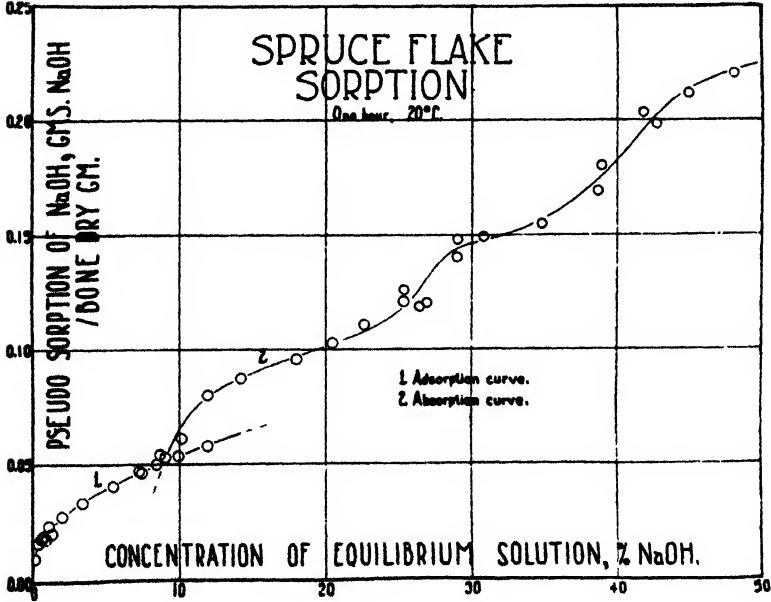


PLATE 4

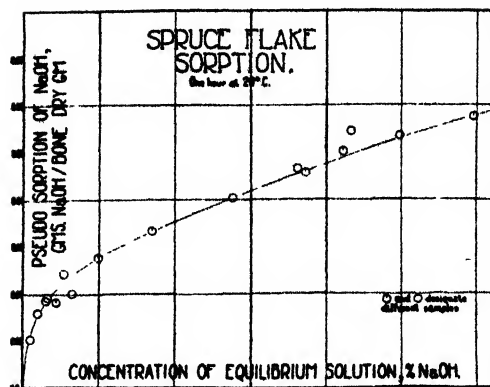


PLATE 5

for adsorption. The phase rule indicates the same general type of curve for absorption as Dalton's law. If compounds are formed the phase rule predicts a step-like diagram. Experimentally the cotton curve appears to be a mean. Perhaps this may be considered somewhat similar in type to the Pd-H₂ sorption curve.

The term solid solution is here used as a partial synonym for absorption, to forcibly denote that the effect is internal in nature and to recall simultaneously that the curves have some theoretical basis in the phase rule and Dalton's law. The other laws of solid solutions may or may not be observed. It will require further work to settle these points. The precise configuration of alkali

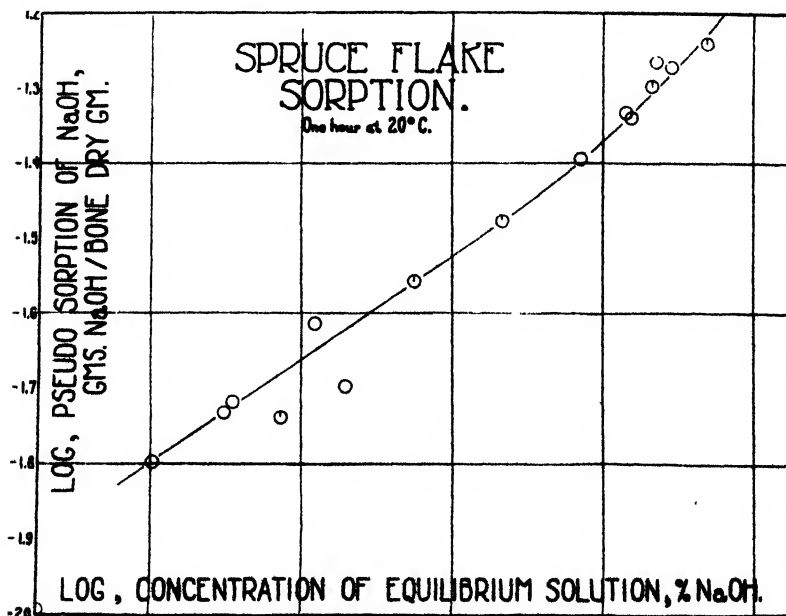


PLATE 6

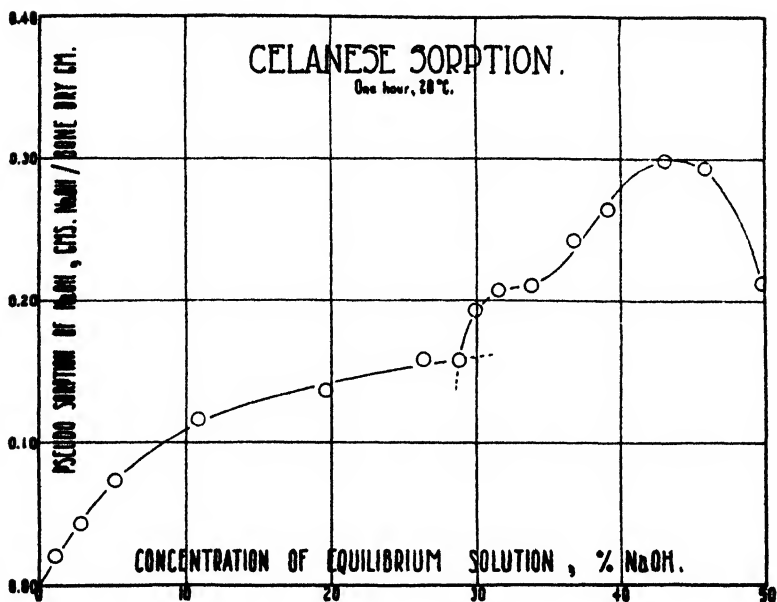


PLATE 7

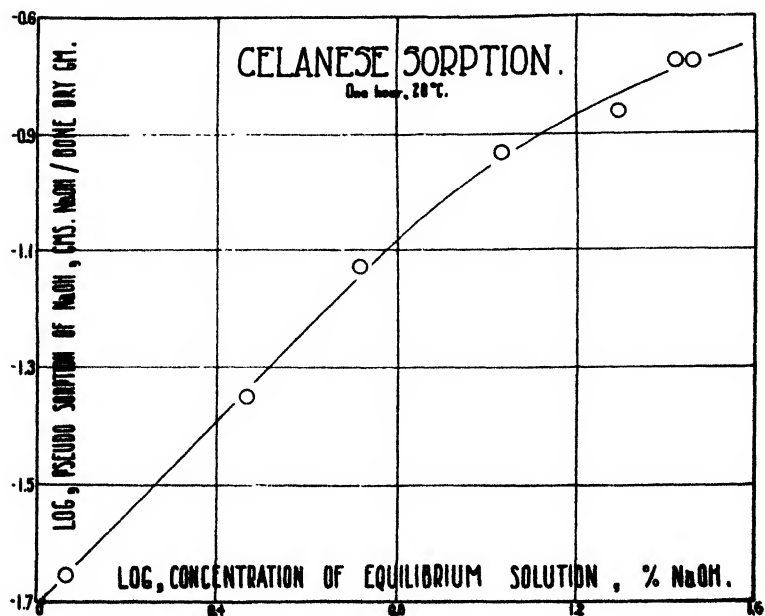


PLATE 8

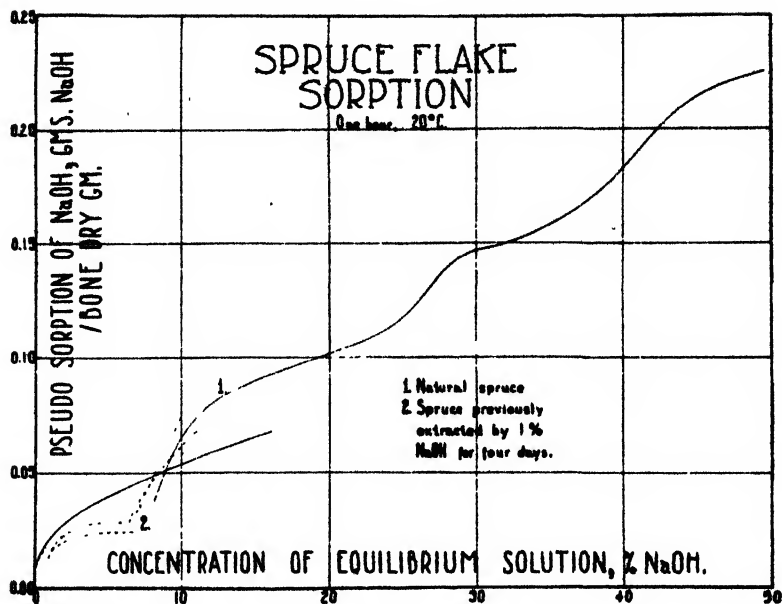


PLATE 9

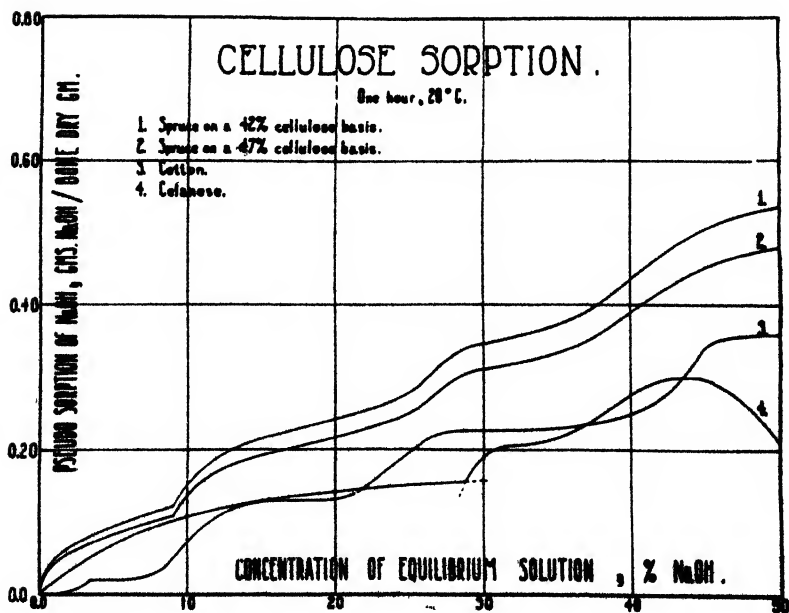


PLATE 10

and water in the cellulose crystal is not suggested. The term internal concentration may be substituted, or the original term absorption even may be considered of sufficient strength. A lucid portrayal of facts is desired more than anything else. Suggestions of more appropriate terms would be welcomed.

It should not be forgotten that the generally accepted explanation of the horizontal portions of the step-like cotton diagram as being due to compound formation may be entirely fallacious. The step-like diagram may be possibly due to a greater adsorbing area being produced by swelling actions occurring at critical concentrations. This viewpoint would eliminate absorption and attribute all curves to the effect of adsorption but on varying surface areas.

The remaining plates show the effect of the source of the cellulose on the sorption curves. Below approximately 10% for wood and 30% for "Celanese" the type of curve obtained is likely due to adsorption. These curves obey Freundlich's adsorption isotherm as shown by the straight line logarithmic plots of these curves below the critical concentrations just named. Plates number 6 and 8.

Work on cellophane is progressing. It is planned to complete this curve and obtain curves for rayon and viscose silk from cotton. The cotton curve at intermediate concentrations is to be reconsidered especially with regard to purified samples of various origins. When this work is finished it is hoped the interpretations of the curves will be more conclusive.

The planned work would include desorption measurement. A few of these have been made already.

It should be pointed out from Plate 10 that all these curves can be approximately represented by straight lines.

Each curve can be replaced by one straight line as a first approximation. The constant sorption differentials or tangents of each of these lines are given.

Spruce, on a basis of 44.5 % cellulose

= 0.010 g NaOH per g cellulose per % of conc. change in the solution

Cotton

= 0.070 g " cellulose " "

Celanese

= 0.066 g " " " "

Spruce, on a basis of total wood content

= 0.048 g NaOH per g wood per % of conc. change.

These relations may eventually evolve a substantial theory.

Various theories of adsorption and combination have been put forward by many workers in this field to explain alkali-cellulose affinity. Which name adsorption or combination is applied to this affinity is of little import as these terms merge into each other. The effect dealt with is certainly on the border line.

When this work is finished it is hoped the interpretation of the curves will be more conclusive.

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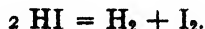
THE DECOMPOSITION OF DIMETHYL ETHER ON THE SURFACE OF PLATINUM

BY E. W. R. STEACIE AND H. A. REEVE

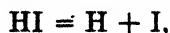
Introduction

It is of considerable interest to compare the velocities of homogeneous and heterogeneous gas reactions. In this connection it has been shown by Hinshelwood that there is a general tendency for homogeneous bimolecular reactions to become unimolecular on the surface of a catalyst, the heat of activation of the reaction falling to about one-half of its former value. This change in the characteristics of the reaction is accompanied by a modification of the reaction path.

The homogeneous decomposition of hydrogen iodide, for example, proceeds as indicated by the equation



The possible homogeneous unimolecular decomposition



followed by a subsequent recombination of the atoms, is ruled out since the formation of atomic hydrogen would be a highly endothermic process. The momentary concentration of a large amount of energy in the molecule would thus be necessary, and hence a very large heat of activation would be associated with the reaction. The presence of a metal surface, however, renders such a change possible since the atomic hydrogen and iodine formed can be held on the surface in an adsorbed condition, and later the atoms evaporate in pairs as molecular hydrogen and iodine.

The heat of activation of the homogeneous bimolecular decomposition is 44,000 calories per gram molecule.¹ In order that two molecules may decompose, they must therefore have a combined energy in excess of 44,000 calories. For the heterogeneous unimolecular decomposition on the surface of gold the heat of activation is 25,000 calories.² Hence one molecule in order to decompose must have an energy in excess of 25,000 calories. The lowering of the activation energy by the catalyst is therefore accompanied by a change in the mechanism of the reaction, in the one case only a single molecule being activated, while in the other case two molecules must be activated simultaneously. In consequence the effect of the catalyst on the magnitude of the activation energy is left unanswered.

¹ Bodenstein: *Z. physik. Chem.*, **29**, 295 (1899).

² Hinshelwood: *J. Chem. Soc.*, **127**, 1552 (1925).

It is therefore of interest to compare the homogeneous and heterogeneous reactions in the case of a substance which decomposes homogeneously in a unimolecular manner. Previous investigations of this kind have been made with acetone,³ ethyl ether,⁴ and propionaldehyde.⁵ The present paper deals with a similar investigation using methyl ether on the surface of platinum.

Methods of investigating Heterogeneous Gas Reactions. There are two main methods of investigating heterogeneous gas reactions.

(a) The catalyst is contained in a bulb in finely divided form. The reactant, or reactants, is admitted to the bulb, or passed through it continuously, and the reaction is followed by the pressure change which accompanies it or by analysis. This method is the simpler of the two, and is the more usual when the course of the reaction, yield, etc., is of primary importance. On account of the lack of definite knowledge of the surface, etc. it is not a suitable method of investigating the molecular statistics of the reaction.

(b) The catalyst consists of a fine filament stretched axially through the reaction vessel. The vessel containing the gas is kept at or near room temperature, while the filament is heated electrically to the desired temperature. This method is by far the most suitable when an accurate knowledge of the molecular statistics of the reaction is desired, and is the one used in this case. In this method the solid material

can function in two ways, either by adsorbing the reactant and permitting a catalytic reaction, or else by merely acting as a source of energy. In the latter case the question of energy transfer between gas molecules and the solid surface will be of paramount importance.

Apparatus. The apparatus was similar, with the exception of the electrical set-up, to that used in previous investigations. It consisted of a reaction bulb of about 100 cc capacity, through which a platinum wire (0.05 to 0.10 mm diameter) was sealed axially. The bulb was connected by capillary tubing and stopcocks to a capillary manometer, a supply of methyl ether, and a pumping system. The connecting tubing was wound with nichrome wire and heated electrically to prevent condensation. The reaction bulb was immersed in an oil bath, which was maintained at 45°C.

Temperature Measurement and Control. The temperature of the heated filament was obtained from its resistance in the following manner. The filament A (Fig. 1) was made one arm of a Wheatstone Bridge ABCD. Since

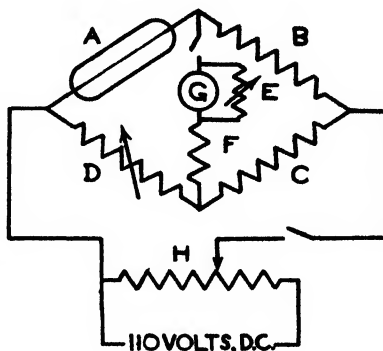


FIG. 1
Electrical Diagram

³ Taylor: J. Phys. Chem., 33, 1793 (1929).

⁴ Steacie and Campbell: Proc. Roy. Soc., 128 A, 451 (1930); Taylor and Schwartz: J. Phys. Chem., 35, 1044 (1931).

⁵ Steacie and Morton: Can. J. Research, 4, 582 (1931).

the resistance of the various filaments used was low (from 1 to 15 ohms), the standard resistance *B* was of the same magnitude and was immersed in a large, well-stirred oil-bath. The heating of this resistance was negligible with the current used. Two high resistances, *C* and *D*, were used in the other arm of the bridge. *C* was a standard 10,000 ohm resistance, and *D* was a variable 1/10 to 100,000 ohm, resistance.

A sensitive galvanometer, *G*, was used. The sensitivity could be varied by the resistance *F* in series, or by the variable shunt *E*. The voltage applied to the bridge was regulated by the potentiometer *H*, which was connected directly to the 110 volt D.C. supply.

Methyl ether⁶ was prepared from sulphuric acid and methyl alcohol. The gas was bubbled through sulphuric acid saturated with methyl ether, passed through phosphorus pentoxide tubes, and fractionally distilled. During the course of the experiments it was stored as a liquid in a bulb immersed in a solid carbon dioxide-acetone mixture.

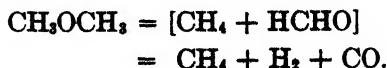
Experimental Procedure

The resistance of the filament was measured at various temperatures, as determined by a Leeds and Northrup optical pyrometer, over a range from 700° to 1100°C, at 50° intervals. A resistance-temperature curve was constructed from these results. On extrapolation this curve gave good agreement with the experimentally determined resistance at room temperature. Even if the absolute values of the temperature of the filament are slightly in error, this will be unimportant for the present purpose provided that the relative temperatures are in good agreement.

During any one run the bridge setting was such that a balance gave a filament resistance corresponding to the temperature desired. On account of the changing thermal conductivity of the gas mixtures, as the reaction progressed, it was necessary to vary the impressed voltage so as to maintain a balance in the bridge circuit.

The reaction was followed by admitting methyl ether to the reaction vessel, maintaining the filament at the desired temperature, and observing the variation of pressure with time.

The Course of the Reaction. Hinshelwood and Askey⁷ found that the homogeneous decomposition of methyl ether was mainly as represented by the equation



Thus in a typical analysis of the products they found 32.0% carbon monoxide, 33.5% hydrogen, and 34.5% methane.

⁶ We are indebted to Mr. J. S. Tapp of this laboratory for supplying the methyl ether used.

⁷ Proc. Roy. Soc., 115 A, 215 (1927).

In the present investigation analysis showed that the reaction was, in the main, the same as the above. Thus a typical analysis at 977°C gave the following result: $\text{CO} = 34.6\%$, $\text{CH}_4 = 33.0\%$, $\text{H}_2 = 32.5\%$.

In the homogeneous reaction, in agreement with the foregoing equation, pressure increases at completion of about 200% were obtained at all temperatures. In this investigation, however, pressure increases at completion of $186 \pm 2\%$ were invariably obtained. This somewhat lower value was undoubtedly due to the condensation of a small amount of paraformaldehyde on the walls of the reaction vessel. Since the final pressure increase was the same at all temperatures, however, it is justifiable to use the pressure increase as a criterion of the extent to which the reaction has progressed. The times for various fractional pressure increases have therefore been used as a measure of the reaction velocity.

Experimental Results

During the course of the investigation a number of different filaments were used. In general these filaments showed considerable differences on account of differing diameter, surface conditions, etc. In the case of a particular filament, after a certain amount of preliminary aging, a steady condition was finally reached and reproducible reaction velocity results could then be obtained. This steady condition might be upset, however, by too drastic heating.

The results given below were obtained on various filaments which had reached a steady condition. In any particular series the runs were made in random order to obviate any error due to aging.

The Effect of Pressure. Fig. 2 shows typical pressure-time curves for various initial pressures at 1150°K, on filament No. 1. The complete data for a typical run are given in Table I.

TABLE I
Filament No. 1. 1150°K

Time mins.	Pressure mm	Per cent decomposed	K
0	316	—	—
3	345	6.0	0.0194
8	412	17.4	0.0239
12	463	26.0	0.0250
17	520	35.8	0.0261
22	568	43.9	0.0262
29	624	53.4	0.0262
35	663	60.0	0.0262
40	692	65.1	0.0264
50	735	72.3	0.0258
60	766	77.5	0.0250

The values of per cent decomposition are calculated on the assumption that an increase in pressure of 186% corresponds to complete decomposition. The constants given in the last column are those calculated for a unimolecular reaction. As in the homogeneous reaction the constants rise in the early stages of the reaction while formaldehyde is accumulating, and finally become constant within the experimental error.

The effect of pressure on the rate of reaction is indicated by Fig. 3 and some typical data are given in Table II. As in the homogeneous reaction the velocity constants fall off at pressures below 300-400 mm.

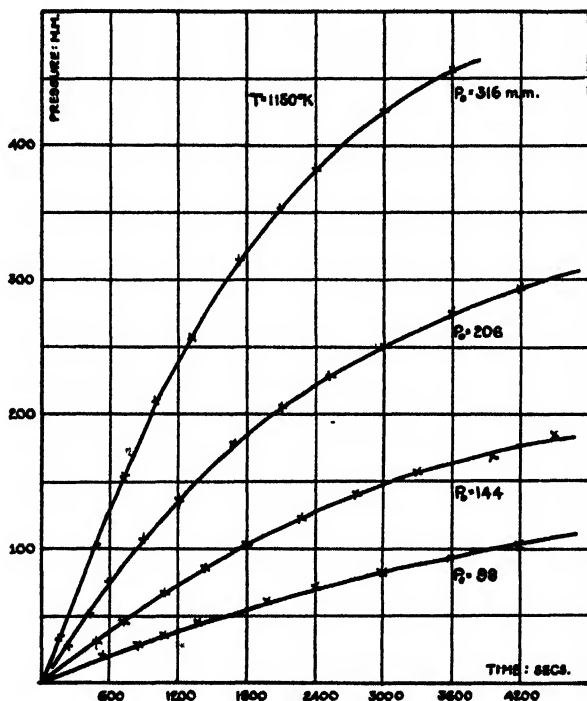


FIG. 2
Pressure-Time Curves

TABLE II
Filament No. 1
Temperature = 1150°K

Pressure mm	T ₅₀ mins.	T ₁₀₀ mins.	Pressure mm	T ₅₀ mins.	T ₁₀₀ mins.
97	23.0	53.6	316	12.0	29.0
98	25.5	64.4	318	12.0	28.3
144	19.3	48.4	430	10.0	23.0
206	14.3	35.3	432	10.7	25.4
314	10.6	25.4	433	10.7	25.4
315	12.6	30.0			

The Temperature Coefficient. The heat of activation was calculated from two entirely separate series of results on different filaments.

In the first series, for experimental reasons, it was impossible to use initial pressures above 400 mm. The heat of activation was therefore calculated by extrapolating the results at each temperature to the high pressure rate.

In the second series of results runs were made at initial pressures of about 700 mm. At these pressures the falling off was negligible and no extrapolation was necessary.

Some typical data for the second series are given in Table III. Fig. 4 shows a plot of $\log T_{25}$, $\log T_{50}$ and $\log T_{100}$ against the reciprocal of the absolute temperature.

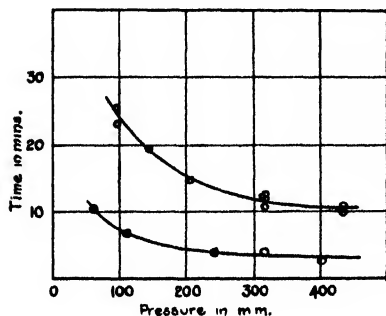


FIG. 3

The Effect of Pressure on the Rate of Reaction

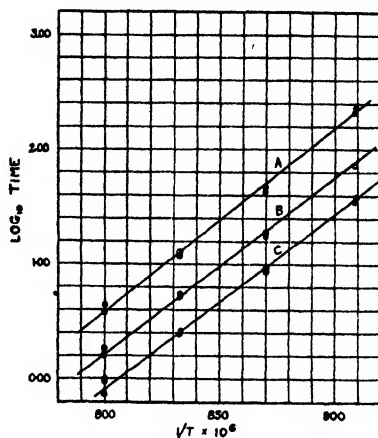


FIG. 4

The Temperature Coefficient

Curve A—Calculated from T_{100}

Curve B—Calculated from T_{50}

Curve C—Calculated from T_{25}

TABLE III

Filament No. 2

Initial pressures ca. 700 mm.

Temperature °K	T_{25} mins.	T_{50} mins.	T_{100} mins.
1100	37.5	74	216
	37.0	74	236
1150	8.75	17.8	43
	9.25	18.5	47
1200	2.53	5.20	12.2
	2.58	5.33	12.5
1250	0.92	1.60	3.84
	0.97	1.87	4.33
	0.73		

The heats of activation calculated for various fractional times for both series of results are given in Table IV.

TABLE IV

Series	Heat of Activation		
	from T_{25}	from T_{50}	from T_{100}
	calories per gram mol.		
1	—	68500	70100
2	68300	69500	72200

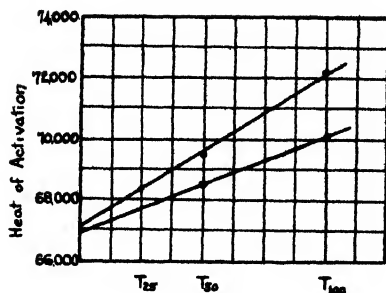


FIG. 5

Extrapolation of the Heat of Activation to Initial Rates

On account of the complication due to the intermediate formation of formaldehyde, the best values of the heat of activation will be obtained by the extrapolation of the above values to initial rates. This is done in Fig. 5. The values obtained in this way for the two series are 66900 and 67100 calories. The mean value of the heat of activation is therefore 67000, as compared with 58500 found by Hinshelwood and Askey for the homogeneous reaction.

Discussion

A comparison of the heats of activation of homogeneous unimolecular decompositions with those of the same reactions in contact with hot filaments shows that the results fall into two classes. The data are summarized in Table V.

TABLE V

Substance	Heat of Activation	
	Homogeneous	Filament
Acetone	68,500	68,400
Ethyl Ether		
(Steacie & Campbell)	53,000	52,000
(Taylor & Schwartz)		57,000
Propionaldehyde	55,000	96,500
Methyl Ether	58,500	67,000

It will be seen that in the first two cases the heats of activation agree within the experimental error, while in the last two the heat of activation of the filament reaction is *higher* than that of the homogeneous reaction. This point will be discussed later in detail.

There are two possible explanations of the action of the filament in these reactions: (a) Molecules are activated by collisions with the filament, statistical redistribution of energy being produced by such collisions. (b) The filament serves as a source of energy, the surrounding gas layer being maintained at a high temperature. Activation takes place in the hot gas layer by ordinary molecular collisions.

The second explanation seems by far the more likely, since it is difficult to see why the velocity constants should fall off at low pressures if collision with the filament were a necessary preliminary to reaction. That this is the correct explanation may be proved conclusively by an examination of the statistics of the reaction.

Some typical data for the decomposition of methyl ether in contact with platinum follow: Filament temperature, 1150°K ; pressure, 316 mm; volume of reaction vessel, 100 cc; filament length, 10 cm; filament diameter, 0.06 mm; bath temperature, 318°K ; rate of decomposition, 0.033% per sec. Whence we obtain: (a) *The number of molecules reacting* which is 3.19×10^{17} molecules per sec. and (b) *The number of molecules hitting the filament*.

According to Knudsen's equation we have

$$m = \sqrt{\frac{M}{2\pi RT}} p,$$

where m is the mass of gas striking the filament per sq. cm. per second, M is the molecular weight, T is the absolute temperature, and p is the pressure in bars. Evaluating the constants, and putting the pressure in atmospheres, we have

$$m = 44.2 \sqrt{M/T} p.$$

The value of T to be used is somewhat uncertain. Since we are only interested in the order of magnitude of the results, it is not of much importance, and the simplest assumption to make is that the temperature of the colliding molecules is that of the filament. In any case an error of even 200° in T will not introduce more than a 10% error into the result.

Whence we have $m = 3.68$ g per sec. per sq. cm., hence the number of molecules striking the filament is 4.85×10^{22} molecules per sq. cm. per sec. The surface area of the filament is 0.188 sq. cm., hence we have *number of molecules striking the filament* = 9.12×10^{21} per second.

(c) *The fraction of the molecules at 1150°K possessing the energy of activation.*

Using Hinshelwood's form of theory, this will be given by

$$\frac{e^{-\frac{E + (\frac{1}{2}n - 1)RT}{RT}} \left(\frac{E + (\frac{1}{2}n - 1)RT}{RT} \right)^{\frac{1}{2}n - 1}}{\frac{1}{2}n - 1}$$

Assuming that the heat of activation found by Hinshelwood and Askey for the homogeneous reaction is the true one, we have $E = 58500$, and $n = \text{ca. } 12$. Whence the fraction of the molecules at 1150°K which possess the energy of activation = 1.36×10^{-8} . Hence the total number of activated molecules, produced by collisions with the filament only is $9.12 \times 10^{21} \times 1.36 \times 10^{-8} = 1.24 \times 10^{14}$ molecules per sec.

Hence about 2600 molecules react for every one which obtains the necessary energy from the filament by direct collision. It may therefore be concluded that the reaction is occurring in a layer of hot gas surrounding the filament. The effective dimensions of this layer may be calculated as follows:

The total number of molecules entering into collisions in the gas per cc per sec. is given by

$$2 \sqrt{2} \pi s^2 u n^2,$$

where s is the molecular diameter, u the root mean square velocity, and n the number of molecules per cc. The total number of activated molecules produced in the gas per cc per sec. is therefore given by

$$\frac{2 \sqrt{2} \pi s^2 u n^2 e^{-\frac{E + (\frac{1}{2}n - 1)RT}{RT}} \left(\frac{E + (\frac{1}{2}n - 1)RT}{RT} \right)^{\frac{1}{2}n - 1}}{\left[\frac{1}{2}n - 1 \right]}$$

In order to evaluate this expression it is necessary to assign a value to s , the molecular diameter. Kinetic theory considerations indicate a value of about 5×10^{-8} cm. It is known, however, that molecules with a high energy content can transfer energy by resonance, and in general in dealing with energy transfers effective diameters much larger than kinetic theory diameters must be used. We may therefore assume $S = 20 \times 10^{-8}$ cm. Whence the number of activated molecules produced by collisions in the gas at 1150°K is 3.54×10^{22} molecules per cc per sec.

The number of molecules reacting per second is 3.19×10^{17} . Hence the effective volume of the space in which reaction occurs is

$$\frac{3.19 \times 10^{17}}{3.54 \times 10^{22}} = 9.00 \times 10^{-6} \text{ cc}$$

Whence the effective thickness of the region surrounding the filament in which reaction occurs is 4.73×10^{-4} mm.*

It is well known that practically the entire temperature drop in the gas surrounding a filament of this type takes place in a "skin" about 0.5 mm thick by conduction. The last few degrees drop is much more gradual, and the heat transfer takes place mainly by convection. The total temperature drop here is 832° . If we assume that 750° of this occurs in such a layer, then the reaction is occurring in a zone surrounding the wire which includes a temperature gradient of about 1° . The volume, however, is a minimum value, as explained before. We may therefore conclude that the zone in which reaction occurs does not include a great enough temperature gradient to introduce any appreciable error into the calculated value of the temperature coefficient of the reaction, *provided that the filament is in thermal equilibrium with the gas.*

Calculations for ethyl ether, acetone, and propionaldehyde yield similar results. In every case it is necessary to assume that the reaction occurs in a hot gas layer surrounding the filament.

We may therefore consider that the dynamics of the decomposition of ethyl ether and of acetone are completely explained. In the case of propional-

* Since this volume is obtained by equating the number of molecules activated to the number reacting, it will be a minimum value. It will, however, be approximately correct since the calculations have been made for a pressure at which the velocity constants have fallen off to an appreciable extent.

dehyde and of methyl ether, however, it is still necessary to explain the fact that the temperature coefficients are higher than those of the homogeneous reactions. The heats of activation calculated for the filament reactions cannot be the true ones. Thus for propionaldehyde calculation shows that if the true value of E were 96,500 calories, then even if the whole reaction vessel were at the temperature of the filament the rate would still be 167 times slower than the observed value.

The only possible explanation of the high temperature coefficients of these reactions would seem to involve the transfer of energy between the filament and incident gas molecules.

Energy Transfer between Gas Molecules and the Filament. By means of heat conductivity measurements at low pressures Soddy and Berry⁸ came to the conclusion the accommodation coefficient for gases of high molecular weight was always in the neighbourhood of unity. Langmuir's theory of adsorption indicates that all, or nearly all, the molecules hitting a solid condense and reëvaporate. The accommodation coefficients are therefore virtually unity, and almost all the molecules leave in thermal equilibrium with the filament. This conclusion has been supported by a number of investigations. Recently, however, it has been shown that in certain cases molecular or atomic beams may be reflected specularly from solid surfaces without any transfer of energy.⁹

It therefore seems plausible to assume that energy transfer between complex gas molecules and solids may be highly specific, and that in certain cases the accommodation coefficients may be quite low. This is especially so in the case of molecules which decompose unimolecularly, since such molecules are notoriously specific in action insofar as the transfer of energy is concerned.

The mechanism of the foregoing reactions may therefore be explained on the following basis. With acetone and ethyl ether the molecules are mostly adsorbed on collision. They evaporate after a very short mean life on the surface, and therefore leave in thermal equilibrium with the surface. The inner side of the gas layer next to the filament is therefore at a temperature which does not differ appreciably from the temperature of the filament. No appreciable error is therefore introduced into the calculation of the heat of activation of the reaction. With propionaldehyde and methyl ether the accommodation coefficients may be assumed to be low. (This assumption will be discussed later). Hence comparatively few of the molecules are adsorbed and reach thermal equilibrium with the filament. The majority of the molecules are reflected more or less specularly and very little energy is transferred to them. There is therefore a very abrupt drop in temperature at the surface of the wire, followed by the usual more gradual skin effect. If this assumption is correct, the mean temperature of the layer in which reaction occurs will be considerably below the temperature of the filament itself.

The high temperature coefficient of the reaction may therefore be explained in two ways: (a) We may interpret the high temperature coefficient as being due solely to the cause mentioned above. The temperature scale used in

⁸ Proc. Roy. Soc., **84 A**, 576 (1911).

⁹ Bradley: Chem. Rev., **9**, 47 (1931).

calculating the heat of activation of the reaction should therefore be shifted to somewhat lower temperatures. The heat of activation of the reaction is inversely proportional to $(1/T_1 - 1/T_2)$. If we lower both temperatures by a constant amount, the calculated value of the heat of activation will therefore decrease. To explain the difference in the heats of activation on this ground alone would require a very large temperature drop at the surface of the filament (for propionaldehyde 275°C). It seems much more likely that the following explanation is the true one. (b) It has been observed that accommodation coefficients increase with increasing temperature. We may therefore explain the high temperature coefficient of the reaction in a much more reasonable way by assuming that the accommodation coefficients are low, but not excessively low, and vary with temperature. The temperature coefficient of the reaction is therefore a composite one, and includes the temperature coefficient of the accommodation coefficient. It is thus unnecessary to assume such a pronounced drop in temperature at the surface of the filament.

The specific action of the surface remains to be explained. If the foregoing assumptions are valid, the accommodation coefficients for ethyl ether and acetone are near unity while those for propionaldehyde and methyl ether are quite low. Accommodation coefficients usually rise in the presence of a layer of adsorbed gas. It is therefore by no means improbable that the specific action depends on the relative adsorption of the various products formed in the decompositions. It has been noticed that a small amount of carbon is deposited in the decomposition of propionaldehyde and of methyl ether, but not in the other cases. This would seem to be the most likely explanation of the specificity.

A number of the questions raised above might be settled by a determination of the heat loss from filaments in the presence of the various gases. Such experiments are in progress.

Summary

The kinetics of the thermal decomposition of gaseous dimethyl ether in contact with heated platinum filaments have been investigated. The decomposition is unimolecular and occurs in a hot gas layer surrounding the filament. The heat of activation is found to be 67,000 calories as compared with 58,500 for the homogeneous reaction. The high temperature coefficient may be explained on the assumption that the accommodation coefficient is low, and hence thermal equilibrium with the filament is not attained by colliding gas molecules.

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COLLOIDAL BORON

BY ALBERT L. ELDER AND NAOMA D. GREEN

Svedberg¹ reports that colloidal boron has been known nearly as long as amorphous boron. Kuzel² was granted patents for the preparation of colloidal boron. Ageno and Barzette³ have contributed to the study of colloidal boron. A more extended report was given by Gutbier⁴ who prepared sols by reduction of B_2O_3 with Mg, Na, and K. The fusion mixture was purified by treatment with dilute and conc. HCl followed by washing with distilled water until the material which went through the filter was in a colloidal state. His failure to obtain consistent results suggested the possibility of continuing this investigation. Sols prepared using identical procedure by Astfalk and Boss under his direction varied greatly in rate of settling, stability under dialysis, color, rate of flocculation with electrolytes. They recognize that the colloidal boron was not pure boron.

Our preliminary experiments using the procedure outlined by Gutbier gave negative results or at best extremely dilute sols. The general procedure was the fusion of Mg and B_2O_3 in approximately the ratio of 1 to 3. The fused mixture was cooled, pulverized, treated with conc. HCl, and washed on a suction filter with hot distilled water. An extremely dilute sol was sometimes obtained on long washing. Further washing yielded no sol.

In an attempt to prepare a more concentrated sol fusions containing Mg and B_2O_3 in ratios varying from 1 to 10 to 10 to 1 were made. The most concentrated sol was with a mixture of Mg and B_2O_3 in the ratio 1 to 3. It was discovered that refluxing from 0.5 to 1 g of dried purified boron with 100 to 250 cc of distilled water for from 2 to 2.5 hours gave on filtration much more concentrated sols.

The fusion container was an open iron vessel 8.5 cm deep by 4 cm in diameter having walls 4 mm thick. The reaction was started by the use of two oxygen-gas blast lamps which were focused on the lower part of the container. To insure rapid fusion the time of heating was less than five minutes. The reaction once started is very vigorous. It is advisable to grind the fused, cooled mass before treating with conc. HCl.

The addition to the fusion mixture of certain impurities which might have been found in the raw materials of previous investigators altered the concentration of the colloidal material. For example the addition of Na_2SO_4 in concentration of 0.01 and 0.001% of B_2O_3 by weight caused definite increase in the concentration of sols obtained. $NaNO_3$ and NaCl in equivalent concentrations were not as effective as Na_2SO_4 . The addition of traces of iron filings to the fusion mixture increased the concentration of the sol.

¹ Gutbier: *Kolloid-Z.*, **13**, 137 (1914).

² British Pat., 25,864; French Pat., 371,799; German Pat., 197,379; C. A., **1**, 1930 (1906).

³ Atti. Accad. Lincei, **1**, 1824 (1910).

⁴ *Kolloid-Z.*, **13**, 137 (1914).

Study was made of some of the properties of these sols. The sols prepared by refluxing were found by electrophoresis measurements to be electro-negative. The acid sols were coagulated very quickly when subjected to 220 volt potential while the neutral sols were not. Since the colloidal boron was prepared by refluxing the fusion residue with boiling water the sols are obviously rather insensitive to coagulation by heat.

In contrast with the colloidal solutions of boron reported by Gutbier¹ and others² the sols prepared in these experiments were extremely resistant to coagulation by electrolytes. HCl, 1 N $\text{Al}_2(\text{SO}_4)_3$, 1 N CaCl_2 and 1 N NaCl gave no decisive coagulation in any concentrations. The addition of crystals of $\text{Al}_2(\text{SO}_4)_3$ and of SnCl_4 was effective only in exceedingly high concentrations.

Mixing boron and iron sols caused complete coagulation of both. The concentration of iron in the iron sol used was 4.27×10^{-4} g/cc. One cc of the iron sol coagulated 3 cc of boron sol in one hour. The concentration of solid matter in the boron sol was 0.052% of the total weight. On ultrafiltration of this sol, and evaporation of the ultrafiltrate a residue of 0.017% was obtained. This indicates that it was the electrolyte present in the boron sol which coagulated the iron sol which in turn carried down with it the colloidal boron. The boron sol ultrafiltrate was effective in equivalent concentration in coagulating the $\text{Fe}(\text{OH})_3$ sol.

All attempts at concentration of the boron sol by pervaporation and dialysis were unsuccessful. Attempts to stabilize the sol by addition of gelatin solution to give total gelatin concentrations of 0.02% to 0.4%, as well as soap solution to a concentration of 0.4% and of a trace of zinc ammonium alginate were unsuccessful. The addition of a trace of glycol bori-borate had some effect in slowing the rate of sedimentation.

The rate of settling in refluxed sols was much slower than that in sols prepared by direct washing. Most of the sedimentation in the first case took place in from one week to two or three months and in the second case always within four days.

A brief study of the preparation of boron sols by the reduction of B_2O_3 with Na showed the sols to be similar to those described above but blue or bluish green in contrast with the yellowish brown sols obtained from the Mg reduction. The stability of these sols was increased from several hours to three months by refluxing although the concentration was not greatly increased.

The following results are indicative of the adsorptive capacity of the boron used. Percent adsorption by weight, ethyl acetate 17.5, acetone 20.8, benzene 14.3, ethyl alcohol 8.7, water 7.6.

Summary

A method for the preparation of and some of the properties of colloidal boron are described.

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¹ Kolloid-Z., 13, 137 (1914).

² Ageno and Barzetti: Atti. Accad. Lincei, (5) 1, 1824 (1910).

A NEW THEORY OF EMULSIONS

BY C. H. M. ROBERTS

An emulsion, as is well known, consists of a stable dispersion of one liquid in another liquid. The factors which appear indispensable for the formation of an emulsion are, first, that the two liquids be mutually immiscible; second, that there be suitable agitation to cause the dispersion of one liquid in the other; and third, that there be present in one liquid—or in both—some substance or substances which have the property of protecting the liquid-liquid interface, so as to prevent contact and coalescence of the droplets of the dispersed phase. In general, it is considered that this material, which is called the emulsifying agent, is present in the continuous phase of the emulsion. The approximate truth of these generalisations has been amply demonstrated and may be accepted without question. The problem of emulsions, then, resolves itself chiefly into the determination of the physical characteristics, chemical composition, and mode of operation of the emulsifying agent.

As to the physical characteristics of the emulsifying agent, it has been rather generally considered that the material is colloiddally dispersed in the continuous phase of the system, altho this is by no means a hard and fast rule, since it has been demonstrated that emulsions can be stabilized, on the one hand, by molecularly dispersed materials and, on the other hand, by finely ground solids, whose sizes are much greater than the upper limits usually given for colloidal dispersions.¹ As to the composition of materials suitable for stabilizing emulsions, practically any material may be employed, with suitable combinations of the two primary liquids, the only requirement being that it shall be soluble, dispersible or wettable in or by one of the liquids. As to the mode of operation of the emulsifying agent, it is generally considered that it functions by being adsorbed at the liquid-liquid interface, on the side exposed to the continuous phase, and thereby prevents contact and coalescence of the droplets of the dispersed phase.

Numerous theories have been advanced, from time to time, to explain the observed facts as to the formation and stabilization of emulsions, but these theories are too well known to require extensive consideration at this time.² The *phase-volume* theory of Ostwald presumed that the type of emulsion—that is, oil-in-water or water-in-oil—was related to the percentages of the two phases present. This theory is no longer considered valid. The *viscosity theory* of emulsions has been tested and found wanting and it is now believed that viscosity is a factor which affects emulsions principally by hindering

¹ Holmes: J. Phys. Chem., 29, 1205 (1925).

² Clayton: "Theory of Emulsions," Chap. 3, (1928).

coalescence of the dispersed droplets.³ In this connection, Wilson and Ries⁴ have shown that interfacial films may have viscosity characteristics which enable them to be considered as plastic solids. The question of viscosity therefore must be considered in relation to the interfacial zone, as well as to the liquid phases. The *hydration theory* of Fischer presumes that the emulsifying agent forms, with the continuous phase, a hydration compound, in which the other phase is dispersed. This theory is inadequate to explain some of the observed facts and is in conflict with other observed facts. It cannot, therefore, be considered an adequate theory of emulsions. The *surface tension theory*, or more properly the *interfacial tension theory*, has been extensively investigated and has been found adequate to explain the formation and stability of many emulsions. This theory has merged into the more modern and more widely accepted *adsorption-film theory*, which explains the formation and stability of emulsions on the basis of the formation and stability of an adsorbed film at the interface. A modification of the adsorption-film theory was presented before the First Colloid Symposium, by Finkle, Draper and Hildebrand.⁵ Their theory was based upon the work of Harkins and Langmuir, who proved the oriented adsorption of polar molecules at interfaces and who advanced the idea that there is a relation between the shape of the adsorbed molecules and the degree and direction of curvature of the interface. The factors of angle of contact and electrical characteristics of the adsorbed materials also enter into various theories.

From this very brief and inadequate summary of former theories of emulsions, we will now proceed to a consideration of the new theory to be presented. This theory has been developed, in connection with an exhaustive study of petroleum emulsions, because existing theories have been found inadequate to explain many of the relations found, and is the result of more than eight years' intensive investigation of such emulsions, both in the laboratory and in the field. While petroleum emulsions are predominantly of the water-in-oil type, there are, however, natural petroleum emulsions of the reverse type. Consequently, the theory has had to consider both types and has had to be developed in spite of the very meager information as to the chemical composition and physical properties of the materials entering into such emulsions.

Considering oils as a broad class of materials, it may be said that they consist of a complex mixture of liquid molecules of low polar moment, in which are dissolved or dispersed greater or less amounts of materials of higher polar moments and that some or all of these materials undergo a greater or less degree of ionization. Such a definition can, it is believed, be considered to broadly cover any non-aqueous solution. Previous experience and general

³ It must be appreciated, of course, that the effect of viscosity is more far-reaching than is here indicated. Viscosity enters into the mechanism of emulsion-formation, by decreasing the speed of adsorption; as well as into the mechanism of emulsion-resolution, by decreasing the mobility of the droplets of the dispersed phase, as well as hindering their close approach and coalescence.

⁴ Colloid Symposium Monograph, 1, 145 (1923).

⁵ Colloid Symposium Monograph, 1, 196 (1923).

knowledge indicate that it is the relatively highly polar and ionized constituents of these oils which are of most importance in determining the emulsification characteristics of an oil.

Considering the brines, associated with crude oils, as a broad class and having in mind the high ionizing power of water as a solvent, it may be said that they are complex mixtures of dissolved salts, which are, in general, highly ionized. There may also be present, in this aqueous solution, more or less dissolved or dispersed organic material, which will be relatively highly polar and may be more or less ionized. Such a definition can, it is believed, be considered to cover broadly any aqueous solution. The emulsification characteristics of the aqueous phase will, therefore, depend upon the kinds and concentrations of ions and polar molecules present.

With reference to the effects of ions, Michaelis⁶ makes the very simple assumption that hydroxyl ions are more capillary active than hydrogen ions. Since both these ions have the same magnitude of charge (altho of different sign), while their masses differ greatly, it seems reasonable to extend Michaelis' assumption and to say that the adsorbability of ions at free surfaces increases as their charge to mass ratio decreases. It is, of course, understood that the ions are, probably in all cases, more or less hydrated, which serves to increase their effective mass and may decrease their effective charge. This assumption serves to explain the observed facts that a free distilled-water surface displays a negative charge and that the magnitude and sign of charge of the free surface of aqueous solutions depends upon the concentration and kinds of ions present in solution. The observed great effect of hydrogen and hydroxyl ions on the surface charge, as discussed by Michaelis,⁶ also serves to indicate the importance of pH of the aqueous phase of emulsions.

Especially in connection with adsorption at free liquid surfaces, it is impossible to ascribe attractive forces to a mathematical surface. Therefore the explanation of Michaelis,⁶ that such adsorption is "apparent" and arises from the forces acting within the liquid, is believed to be entirely acceptable. Another way of looking at the question is that such adsorption is due to "rejection" of the adsorbed material from the body of the liquid, the material "rejected" being that which has the lowest charge to mass ratio. Incidentally, the concentration of such material at the surface will accomplish the maximum reduction of surface energy, which is a basic principle of physical chemistry. Adsorption at free liquid surfaces may, therefore, be ascribed to an "exclusion effect," whereby the material is pushed to the surface because it is attracted back into the mass of the system with less force than acts on the other constituents of the system.

The conclusion of the preceding paragraph, as will be immediately apparent, is exactly parallel to the "attraction intensity" principle of Traube.⁷ From Traube's principle, we see that adsorption increases with decreased attraction intensity toward the body of the solution and with increased attrac-

⁶ Alexander's "Colloid Chemistry," 1, 497 (1926); see, also, "Hydrogen Ion Concentration," Chap. X (1926).

⁷ Alexander's "Colloid Chemistry," 1, 640 (1926).

tion intensity toward the adsorbent. This principle is adhered to in developing the characteristics of adsorption at interfaces.

The above discussion has been more or less restricted to ion adsorption, while it is also necessary to consider molecule adsorption. Molecules of all substances have greater or less external electromagnetic fields, which arise from the presence and motion of positive and negative charges in the atoms composing the molecules. According to the dissymmetry of distribution and the characteristics of motion of these charges within the molecule, it will be more or less polar, that is, it will have definite electric and magnetic moments. This has previously been discussed by Harkins.⁸ While a molecule contains exactly equivalent amounts of positive and negative charges and is, therefore, exactly neutral, the unsymmetrical distribution of those charges gives the same external effect as though the molecule was positively charged at one end and negatively charged at the other. It may therefore be considered analogous to a pair of ions very close together and constrained to move as a unit but, with reference to either end, as having a small charge. We may, therefore, as for ions, speak of the charge to mass ratio of molecules and it is evident that, even for highly polar molecules, the ratio is extremely small, as compared to that of ions of even very large mass. In addition, the strong portion of the external field of a polar molecule extends over a very small space (comparable to molecular dimensions) and outside of this space the molecule acts as though it were practically neutral; whereas this is not at all true for ions.⁹

From the above considerations, it follows that polar molecules will adsorb at a free surface in preference to ions, since the surface energy is thereby decreased to a greater extent. Due to the vector character of the fields of polar molecules, it also follows that they will orient in a free surface so as to expose their least polar portions. It may be noted that the fields of ions are vectorial and that adsorbed ions will also be oriented. Since both polar molecules and ions will be present in the same solution, it follows that both the polar molecules and those ions having the lowest charge to mass ratio will tend to accumulate in the surface. That is, there will be competition between ions and molecules for positions in the surface. Since the mobility of ions is much greater than that of molecules, it also seems probable that, when a free surface is suddenly formed, the 'adsorbable' ions will reach that surface considerably in advance of the molecules but will be slowly displaced by polar molecules as the age of the surface increases. That is, in the early stages of adsorption, we may consider the process to be (chiefly) ion adsorption, which is dynamic and reversible and which proceeds toward or to equilibrium; followed by molecular

⁸ Alexander's "Colloid Chemistry," 1, 199 (1926).

⁹ The concept of polar molecules as magnetic dipoles, as well as electric dipoles, while not made use of at this time, is now being investigated. It is mentioned here to call attention to its possible application and will be incorporated into the theory when and if adequate data are obtained. It is obvious that a complete description of the properties of ions and molecules will have to include both their magnetic and electric properties but that this will introduce only such changes into the theory as may be consequences of the relative moments of the two forces. The success of present theories based on electric forces alone indicates that only in relatively few cases will introduction of the magnetic moments necessitate appreciable revisions of theories.

adsorption, which proceeds to equilibrium. In the final state, then, the surface will consist of an equilibrium mixture of "adsorbable" ions and polar molecules, in which the proportion of ions to molecules present will depend upon their relative mobilities, concentrations and the tenacity with which they persist in the surface. In the final state, especially where molecular adsorption is high, it is entirely possible that the surface layer may approach static conditions and become more or less completely irreversible.

The concept of the Helmholtz double layer is adhered to in the present theory. However, the double layer, as is apparent from the preceding discussion, is considered to contain both ions and polar molecules. From the preceding discussion, it is also apparent that the oriented adsorption of polar molecules does not differ at all from the adsorption of layers of ions of opposite polarity, except that in the former case there is a 'rigid' binding between the positive and negative charges at opposite ends of polar molecules, whereas such is not the case where positive and negative ions are concerned. Mooney presented, at the Eighth Colloid Symposium,¹⁰ the concept of the mutual adsorption of ions and molecules, while McBain and Williams, at the Seventh Colloid Symposium,¹¹ presented certain numerical results as to the ratio of ions to molecules adsorbed at free surfaces.

In determination of interfacial potentials, by cataphoretic or streaming potential technique, the new theory proposes that the shear zone, across which the potential difference is measured, is located between the primary, mono-molecular surface layer and the underlying 'diffuse' atmosphere of ions and molecules. This view is taken primarily because of the results of Harkins and others, who have shown that surface layers are usually, if not always, mono-molecular; whereas Fahrenwald¹² and others have shown that surface layers may be poly-molecular. This apparently conflicting evidence may be made concordant by merely assuming that the method of one investigator showed the concentration of material in the primary layer; while that of another showed the total concentration of material in the 'adsorption zone' at the surface. The reason for assuming that the zone of shear does come between the primary, mono-molecular layer and the inner diffuse zone is that, at that place there is the greatest discontinuity of properties between the opposite sides of adjacent layers.¹³ Since it is considered that ions and molecules are mutually adsorbed in a surface, the primary layer is considered to consist of both these components, in proportions dependent upon the previously discussed factors.

To complete this picture of surface adsorption, it may be noted that, in the case of a solution in which negative ions are preferentially adsorbed, while the preferred orientation of polar molecules is with the negative ends exposed, the surface charge will vary, with the age of the surface, from zero to a maximum negative value, corresponding to the (approximate) equilibrium

¹⁰ J. Phys. Chem., **35**, 331 (1931).

¹¹ Colloid Symposium Monograph, **7**, 105 (1930).

¹² Trans. Mining Met. Engrs., **70**, 724 (1924).

¹³ Andrews: Colloid Symposium Monograph, **7**, 119 (1930).

of ion adsorption; thru zero, corresponding to an electrical equivalence between adsorbed ions and adsorbed molecules; to a low positive value, corresponding to an equilibrium of molecular adsorption, in which there is an electrical preponderance of molecules over ions in the surface. It will be seen that this concept permits the explanation of surface charges varying, with time, in both magnitude and sign, without the necessity of postulating different mechanisms of action.

Although it has not been specifically mentioned before, it is to be understood that, in speaking of ions and molecules, those terms refer to ions and molecules in the state of solvation or hydration in which they exist at the place and in the system considered. Each ion and molecule in solution is considered to be the nucleus of an adsorption complex so arranged as to minimize the abruptness of transition of properties between the components of the solution, the effect being entirely analogous to adsorption at interfaces. It is these complexes which adsorb at surfaces or interfaces. Adsorption of these complexes, however, may and probably will result in changes in the solvation conditions and this may be expected to materially alter the characteristics of the boundary layer. There must also be considered the additional probability that physical interaction across the interface will result in further alteration and distortion of these complexes.

The preceding discussion has been directed to a consideration of conditions at a free surface, whereas, in dealing with emulsions, it is necessary to consider conditions at liquid-liquid interfaces. These conditions will now be discussed.

It is known that, usually, in the case of natural brines and oils, the surface energy of the aqueous phase exceeds that of the non-aqueous phase. It therefore follows that the most stable emulsion condition is that in which the aqueous phase forms the dispersed phase of the emulsion. In cases where the reverse condition is true, the aqueous phase forms the continuous phase of the emulsion. There seems to be no reason why this cannot be accepted as generally true for all emulsion systems. From this it follows that the conditions at a water-oil interface, where water is the dispersed phase, are similar to the conditions at a free water surface. That is, the energy level on the water side of the interface is greater than that on the other side. Therefore the character of adsorption on the water side of an interface will be much the same as at a free water surface, except that more-polar materials will concentrate at the interface than at a free surface, since the energy on the other side of the interface is now materially greater than zero, whereas it approaches zero on the air side of a surface. The conditions on the oil side of the interface will, however, be quite different from those at a free surface of the same oil. The energy level on the water side of the interface will now be greater than that on the oil side, instead of (practically) zero, as it is on the air side of a surface. Therefore the adsorption conditions on the oil side of a water-oil interface will be different both in magnitude and kind from those at a free oil surface. Instead of the least polar materials being in the primary layer,

the most polar materials will concentrate there. The conditions may be made somewhat more evident by referring to Fig. 1 in which adsorption at liquid-air and liquid-liquid interfaces is diagrammatically represented.

Another way of arriving at the same conclusions is by the application of the principle stated by Harkins, that adsorption will proceed at an interface in such a manner as to decrease the abruptness of transition of properties from one phase to the other. In the case considered, the energy level in the oil is low, while that in the water is high. Therefore adsorption on the water side will be such as to place the less-polar materials in the water side of the inter-

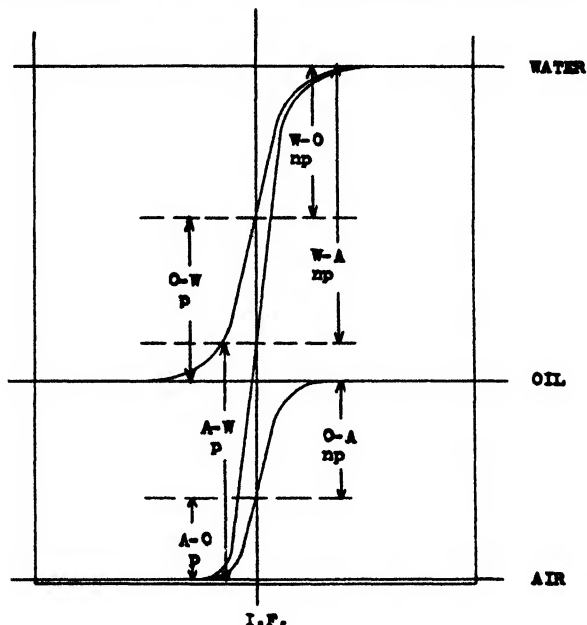


FIG. 1

Diagrammatic Representation of Adsorption at Liquid-Gas and at Liquid-Liquid Interfaces. Horizontal axis represents distance from interface. Vertical axis represents character and intensity of adsorption. Letters in the figure indicate the side of the interface considered, i.e., O-W means the oil side of an oil-water interface, while W-O means the water side of the same interface. The lower case letters are 'p' for polar adsorption and 'np' for non-polar adsorption.

face, while adsorption on the oil side will be such as to place the more-polar materials in the oil side of the interface. It is entirely possible that the difference in character of adsorption at free surfaces and at interfaces may be the cause of the failure of Antonow's law for interfacial tension as a function of the surface tensions of the separate, mutually saturated, phases.

As will be apparent from the foregoing discussion, this theory involves the consideration of adsorption on both sides of an interface. It therefore follows that an interfacial layer must be at least a double mono-molecular layer, providing no interaction occurs between the opposing elements. If such interaction does occur, as for example between hydrogen ions in the primary layer on the water side and fatty acid ions in the primary layer on

the oil side, then a molecule of fatty acid may result, the hydrocarbon end of which is in the oil and the carboxyl end in the water. Such an effect, as is obvious, is quite analogous to the postulated mechanism of contact catalysis. Of course, the same sort of thing may occur, as shown by Harkins, in the case of a molecule in either phase, but partially soluble in the other, without postulating the interaction of ions. Such a condition should give rise to an extremely stable interface and this is known to be the case. If the hydrocarbon end is shorter, making the molecular more polar and more water-soluble, its efficiency as an emulsifying agent should be lower, as is the case. If the hydrocarbon end is much longer, making the molecule less polar and more oil-soluble, its efficiency as an emulsifying agent again decreases. It therefore follows that those fatty acids and their derivatives, whose ratio of polar moment to molecular weight lies between certain limits, should be the most efficient emulsifying agents of their class and this is known to be the case.

At the risk of digressing somewhat from the principal topic of petroleum emulsions, it seems desirable to discuss some phases of the emulsion problem which appear to have offered much difficulty of explanation under prior theories.

There is the problem of antagonistic emulsifiers, of which the case of sodium and calcium oleates has been chosen as an example. We know that sodium oleate stabilizes oil-in-water emulsions, that calcium oleate stabilizes the reverse type, while suitable proportions of the two substances result in no emulsion. The latter condition is the one which requires elucidation. In terms of this theory, calcium oleate in the oil will tend to adsorb on the oil side and will try to pass its polar end into the water, while sodium oleate in the water will tend to adsorb on the water side and will try to pass its non-polar end into the oil. This competition for positions across the interface will actually result in mutual repulsive reactions between the competing molecules, so that neither achieves its purpose, if they happen to be present in a certain proportion, and no emulsion forms. If the proportions differ from the critical, the external phase of the resulting emulsion is the one which contains the excess of soap. It may be noted that repulsive reactions across the interface, between adsorbable ions of like charge, would operate to reduce stability, in a manner similar to that just discussed.

A difficulty of the theory proposed by Finkle, Draper and Hildebrand,⁵ which caused considerable discussion, was the case of an emulsion of benzene in water, with stearic acid in the benzene as the emulsifying agent. This emulsion apparently contradicts the principle that the emulsifying agent should be in the continuous phase. The explanation of the observed facts, under the new theory, is that, although stearic acid is soluble in benzene and is alleged to be insoluble in water, nevertheless, since benzene is extremely non-polar, while the carboxyl end of the acid is highly polar, adsorbed acid molecules project so far into the water phase that it is no stretch of the imagination to consider that they are actually in the water phase, with only their (extreme) ends projecting into the oil. In other words, the acid is

"interfacially" soluble in water, although it may not be appreciably "volumetrically" soluble. This case will now fall nicely into line with Bancroft's principle.

Such an effect as is here postulated may serve at least as a partial explanation of the reversal of some emulsions by agitation. If the solubility is a function of the ratio of exposed surface to total mass, as has been proved in other connections, then it is not hard to see that, since agitation decreases particle size in emulsions and therefore increases this ratio, it may well change the "interfacial" solubility of some materials sufficiently to cause a reversal of emulsion type. In this case, then, the change in emulsion type is really due to an effective change of phase of the dissolved material, even though it is "insoluble" in one phase. Something along the same line is discussed by Taggart,¹⁴ in connection with the degree of solubility of flotation agents. Bartell and Mack¹⁵ also refer to the same sort of thing. They say, "Surface films are of two types, namely; those formed by insoluble highly adsorbed substances and those formed by soluble and less strongly adsorbed substances." The application of the quotation to this portion of the discussion is that the substance, which is presumed to cross the interface into the phase in which it is "insoluble," will be very strongly adsorbed; while that portion of it in the phase in which it is soluble will not be strongly adsorbed. Hence the effective "emulsifying agent" is in the external phase, in accordance with Bancroft's principle.

The question of dual phase emulsions has been extensively investigated, especially by Seifriz,¹⁶ although his results were obtained by the addition of materials to the system, to cause reversal of type. The residues of dispersed oil, within globules of water themselves dispersed in the bulk of the oil, no doubt owe their stability to differences in the emulsifying agent, as Seifriz observes. The present viewpoint relative to dual emulsions, which are sometimes encountered in petroleum systems, considers the case under conditions when there has been no addition of chemicals to the system and when the production conditions are such as to make it fairly certain that the oil and water enter from a single horizon and hence are uniform in composition. The suggested explanation follows from the previous discussion relative to interfacial solubility and the effect on that solubility of alteration of area/mass ratio.

It is known that, when oil and water are agitated together there is a tremendous range of particle sizes produced and there is also considerable dual dispersion. If we assume the case of an emulsifying agent having the "interfacial solubility" postulated, we can easily see that the solubility relations may be sufficiently different on droplets of different sizes, so that the "emulsifying agent" exchanges phases at the interfaces of the smallest droplets and we are left with stable droplets of oil dispersed in water, which is itself dispersed in more of the "same" oil. In connection with natural dual emulsions, it may be

¹⁴ J. Phys. Chem., **36**, 152 (1932).

¹⁵ J. Phys. Chem., **36**, 65 (1932).

¹⁶ J. Phys. Chem., **29**, 738 (1925).

remarked that they are relatively rare, which checks with the low probability of simultaneous occurrence of the necessary combination of properties of oil, water and "emulsifying agent."

To return to the principal topic of discussion, it was previously stated that the problem of emulsions consists chiefly of the determination of the physical characteristics, chemical composition and mode of action of the emulsifying agent, which has usually been considered to be a material present in the external phase of the system. From the preceding discussion, it seems apparent that the emulsifying agent can no longer be considered as a single material in one phase of the system, since the interfacial zone may consist of two Helmholtz "double layers," one in each phase, or it may consist of a "compound" Helmholtz double layer, whose central portion consists of molecules "straddling" the interface. These "straddling" molecules may be formed by interfacial reaction of ions from the two phases or by the "sharing" between phases of molecules partially soluble in both. The problem has therefore become complicated to the extent that the composition of both phases of the system must be subjected to examination, since any component of either phase of the system may, under suitable conditions, aid in stabilizing the interface.

In the study of naturally occurring emulsions in the petroleum industry, the problem is still further complicated by the fact that practically nothing is known about the composition of the various components of the oil phase or what components of that phase contribute to emulsion stability. Considerably more is known about the composition of the aqueous phase of such systems but even that is incomplete and inadequate, since natural brines are usually analysed only for their content of common inorganic constituents. However, it is felt that the situation is by no means hopeless or even very discouraging. There seems no reason to worry excessively over the lack of information as to composition, because it is believed that, whatever the composition, it is the physical properties which determine the emulsification characteristics of the system. Therefore, if those properties, and especially those of the interfacial layer, can be determined, it is believed that sufficient information will have been obtained to enable the essential properties of the emulsion, under changed conditions, to be predicted.

In the light of the foregoing remarks, it is now desired to draw a picture of the mechanism of formation of an emulsion interface, according to the new theory. The formation of a water-in-oil emulsion will be described.

At the instant of formation of an interface, the opposed surfaces of the respective phases will have the same average concentrations of components as any cross-section within the respective volumes; that is, no adsorption has yet taken place. At this instant, also, the electrokinetic potentials on both sides of the interface, by definition, are zero and the interfacial tensions on both sides will have their maximum dynamic values. Ions and molecules immediately begin to move toward the interface, but the ions arrive first because of their higher mobilities. Ions of high polarity tend to accumulate in the interface on the oil side; while ions of low polarity tend to accumulate in the interface on the water side.

Neglecting molecular adsorption for the moment, we can consider that equilibrium of ionic adsorption is attained, at which instant the electrokinetic potentials will have attained maximum values. While this equilibrium is being reached, the interfacial tensions will fall with extreme rapidity, while the electrokinetic potentials will increase with corresponding rapidity.

From this stage of the process we must consider the relatively slow moving molecules, which are beginning to concentrate in the interface and crowd out the more mobile ions. To simplify the picture, we will consider that the aqueous phase consists only of a solution of simple inorganic salts and that no "interfacial compounds" are formed. This enables us to dismiss the water side of the interface from further consideration and leaves that side at the ionic equilibrium stage, with the least polar ions present in the primary layer. On the oil side, the replacement of ions by polar molecules, oriented with their most polar ends toward the water, will proceed continuously. When the point is reached where there is electrical equivalence between the ions and polar molecules on the oil side, the corresponding electrokinetic potential will be zero, while the rate of change of interfacial tension on the oil side will have reached a low value.

As the age of the interface continues to increase beyond this point, there will be an increasing preponderance of molecules over ions in the interface, until the static condition, of a complete mono-molecular layer of polar molecules in the primary layer, is reached. At this time, the electrokinetic potential on the oil side will have attained a low steady value, of opposite sign to that in the early stages of the process, and the interfacial tension will have attained its minimum static value.

It will be noted that attention is repeatedly drawn to the existence of electrokinetic potentials and interfacial tensions on both sides of the interface. This is believed to be entirely valid, even though the primary layer consists of molecules "straddling" the interface, because there are markedly different conditions existing between the primary layer on the oil side and the adjacent oil phase, from those existing between the portions of the corresponding region on the water side. Distinction is made today between electrokinetic potentials in the two phases, although these are commonly measured only for the external phase. From the same point of view, it is entirely probable that, as Bancroft pointed out many years ago, there are two interfacial tensions, one on each side of the interface. These complications in the study of emulsions are unfortunate, but they seem to be inescapable conclusions of the present theory.

Whether or not the conditions of zero potential or reversal of potential, on the oil side, occur as described, obviously depends upon the relative concentrations, polarities, etc., of the adsorbable materials in the oil phase. It may also be pointed out that, if the primary layers on the two sides consist of ions which react to form molecules "straddling" the interface, the progression from ionic to molecular adsorption will occur synchronously with ionic adsorption, despite the fact that there may be no adsorbable polar molecules in the system. It has been pointed out by Clayton,¹⁷ who referred to work of Powis,¹⁸ that electro-

¹⁷ "Theory of Emulsions," 21 (1928).

¹⁸ J. Chem. Soc., 109, 734 (1916).

kinetic potentials at the surface of oil drops dispersed in water decrease with increasing time. The explanation of the effect was not given. In addition, work on certain naturally occurring emulsions, performed in our laboratory, has clearly demonstrated the reversal of potential on the external, oil side of the interface. The emulsions when fresh showed strong negative cataphoresis, which gradually became weaker, then ceased entirely and later changed to weak positive cataphoresis, the whole process requiring about two months for completion. As far as is known, this reversal of interfacial potential in emulsions has not heretofore been observed, would not have been expected under prior theories and could not have been easily explained. The present theory offers a simple explanation of this phenomenon and of that observed by Powis and the observations on reversal of potential were taken as a result of the prediction of the theory that such an effort might occur in certain emulsions. The observations are therefore considered to afford striking confirmation of the essential validity of the theory.

As to the proposition of different interfacial tensions on the two sides of the interface, the situation is more difficult. While it seems entirely probable that this is the case, the measurement of these tensions is more difficult and has not yet been attempted. It is possible that a modification of the sessile drop method could be employed, but it has not seemed profitable for us to attempt it. However, another method of measurement has been used, which, although its true significance has not yet been discovered, has nevertheless yielded results which have shown a surprisingly close correlation with some of the properties of emulsions.

This method involves the measurement of interfacial tension by the ring method and makes use of the excellent correction factors experimentally developed by Harkins.¹⁹ DuNouy²⁰ notes that there is often a difference in the values of interfacial tension, according to whether the ring is pulled from water to oil or pushed from oil to water. The statement is made that the values from oil to water are "too low," but that the values from water to oil "check perfectly even when the ring has passed through the oil before reaching the water." Natural curiosity as to these statements, together with the idea of the existence of different tensions on the two sides of the interface, led to a series of measurements with known liquids. The results were most surprising, in that they showed a high degree of regularity in the sets of measurements, an often large difference between corresponding measurements of "push" and "pull," and an apparently close relation between the measurements in a given direction and the kinds of materials dissolved in the phase into which the ring passed.

The forms of the curves and the values obtained are illustrated in Fig. 2, which shows the results of a series of measurements made with a certain sample of Nujol against distilled water and solutions of sodium chloride, hydrochloric acid and sodium hydroxide. Portions of a single sample of water were used in all cases and the chemicals were the purest obtainable but were

¹⁹ *J. Am. Chem. Soc.*, **52**, 1751 (1930).

²⁰ "Surface Equilibria of Colloids," 173 (1926).

not specially repurified. In each case, the amount used was 5 grams of material, on an anhydrous basis, dissolved in 100 grams of water. The chemicals used were Baker's C. P. Analysed. The water was specially distilled and tested for purity by constancy of surface tension.

As will be seen in the figure, in the case of distilled water, the push and pull values are coincident. In the cases of salt and of acid, the pull values are coincident with the distilled water values, while the push values are materially lower and do not coincide. In the case of caustic soda, the values of both push and pull are materially different from the previous determinations. The

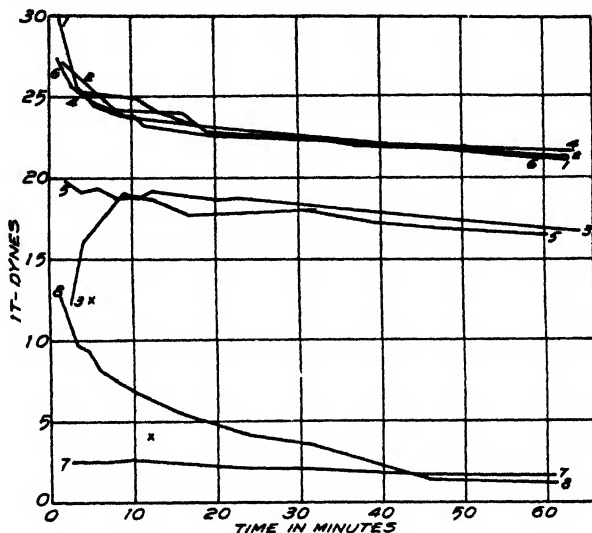


FIG. 2

Interfacial Tensions

NUJOL vs AQUEOUS SOLUTIONS

Odd numbered curves—IT measured by pushing from Oil to Water

Even numbered curves—IT measured by pulling from Water to Oil

Curves 1 and 2—Nujol vs Distilled water Temp. 85°F

" 3 and 4— " " " " plus 5% NaCl " 70°F

" 5 and 6— " " " " " HCl " 72°F

" 7 and 8— " " " " " NaOH " 78°F

Concentration of Solutes—5 g. per 100 g. Water.

Determinations made with DuNouy Interfacial Tensiometer and corrected by use of Harkins' factors (J.A.C.S. 52, 1751).

coincidence of the pull values in every case but the last makes it appear that this measurement indicates something about the conditions in the oil phase, while the push values indicate something about the water phase. As to the case of caustic soda, the natural conclusion is that the Nujol has changed and this is the case, since we had already determined, in an entirely different connection, that caustic soda is quite soluble in Nujol. The large effect of caustic soda on the interfacial tension, which agrees with Fahrenwald's observations²¹ on benzene, but is contrary to Harkins' results²² with benzene, led to discussion

²¹ Trans. Mining Met. Engrs., 70, 682 (1924).

²² J. Am. Chem. Soc., 39, 549 (1917).

of the subject with Dr. Harkins, who suggested the desirability of a check by the drop method. The results of this check are shown by the crosses in the figure, the higher value being for drops whose formation time was five minutes, while the lower was for twelve minute drops; the measurements being for water dropped into oil. While it is recognized that these short times of drop formation probably involve dynamic effects and lack of interfacial equilibrium, the tests nevertheless served the desired purpose of substantiating the results yielded by the ring method and proved that, in this system at least, caustic soda has a large lowering effect. Another test, which attempted to eliminate some of the uncertainty, was made by allowing a partial drop to form and then stand quietly. This drop gradually lengthened and, $3\frac{1}{2}$ minutes after the stop cock had been closed, detached from the dropping tip. It therefore seems quite evident that the interfacial tension was actually and considerably lowered by the caustic soda.

From these and hundreds of other similar measurements, both on controlled systems and on natural brine-oil systems, it is apparent that there is no reason for calling a set of "pull" measurements correct and a set of "push" measurements incorrect or low. As a matter of fact, it is not at all uncommon, especially with natural oils and brines, to find ratios of push to pull values which vary from 10/1 to 1/10, or which, in a given system vary, with time, in the same manner. It therefore appears that there is a place for both types of measurement, that they have a real significance and that they are related, in some manner yet to be discovered, to the adsorption conditions on the two sides of the interface. In view of the simplicity of the measurements, they seem to offer a fruitful field for investigation and it is rather astonishing that results such as these have not been published before.

One obvious difficulty with the measurements is, of course, as was pointed out by Dr. Harkins, the question of relative wettability of the platinum ring by the two liquids. It is planned to repeat certain series of these measurements, using pyrex glass rings, which have recently been constructed. Preliminary measurements of surface and interfacial tensions, using both platinum and pyrex rings, can, however, be reported at this time.

Surface tensions of water, benzol and Nujol give values agreeing closer than one percent, from which it may be concluded that contact angles do not enter appreciably into such measurements. This is in agreement with the known reliability of platinum ring measurements of surface tension of the most diverse materials. It also is in agreement with Harkins's views, as expressed in his paper concerning the ring method for surface and interfacial tension.²³

Interfacial tensions, both push and pull, for the system distilled water-Nujol, have been made, using both types of rings. The values measured from water to oil show excellent agreement, whereas the values measured from oil to water differ by nearly fifty percent. The scope of the measurements is not sufficient to warrant any conclusions at this time, but it is believed that the

²³ J. Am. Chem. Soc., 52, 1770 (1930).

effects may be referable to differences in surface energy relations platinum-oil and platinum-water, as compared to the relations glass-oil and glass-water. If this is at all correct, it may be expected that interfacial tension measurements, relatively free from angle of contact effects, may be expected from rings whose surface energy is either very low or very high, as compared to those of the materials whose interfacial tensions are to be measured. A series of measurements, with rings of different materials, will be made in the near future, in an effort to discover something definite about these relations. It is also suggested that information as to surface energy characteristics of solids may possibly be deduced from such interfacial tension measurements, in a fixed oil-water system, using rings, discs, knife edges, etc., of various materials.

A consideration of the observed facts of the dependence of interfacial potential on the age of an interface, in a given emulsion system, and of the reversal of sign of potential in some emulsions, leads to the conclusion that the stability of an emulsion interface is not necessarily related to the potential. This is in at least qualitative agreement with the observed lack of relation, in many cases, between the stability of emulsions and the interfacial potential and the fact that some emulsions and colloidal dispersions fail to coagulate at zero or at the so-called critical potential. From the present theory, it is apparent that decrease of potential to zero or even its reversal is in no way related, necessarily, to a decrease in stability or thickness of the interfacial layer, a condition precedent to coalescence, but, on the contrary, may be associated with a considerable increase in the stability of the interface. The present theory makes such phenomena understandable without the necessity for recourse to the theory of critical hydration or solvation conditions and is therefore a desirable simplification in dealing with colloids and emulsions.²⁴

The theory of critical hydration, as well as critical potential conditions, as discussed by Kruyt,²⁴ shows that hydrophobe sols are sensitive to ion concentration, while hydrophile sols are insensitive to ion concentration but are sensitive to the action of dehydrating agents. In terms of the present theory, it is suggested that hydrophobe sols owe their stability to ion adsorption and therefore are sensitive to changes in ion concentration; while hydrophile sols owe their stability to molecular adsorption and therefore are insensitive to changes in ion concentration. Another way of expressing it would be that hydrophobe sols are more polar than the dispersion medium and adsorb ions and molecules (with their more polar ends turned toward the particle), hence such sols should be sensitive to changes in concentration of materials which furnish adsorbable materials of high polarity but which are "antagonistic" to the materials already at the interface. Hydrophile sols, on the other hand, would be less polar than the dispersion medium and would tend to adsorb its least polar constituents. They would, therefore, be sensitive only to changes in concentration of materials which furnish adsorbable materials of low polarity and which are "antagonistic" to the materials already at the interface.

Inasmuch as the previous discussion has considered the conditions of adsorption at free surfaces and at liquid-liquid interfaces and since the general

²⁴ Kruyt: Alexander's "Colloid Chemistry," 1, 306 (1926).

problem of emulsions of necessity involves, in addition, the action of dispersed solids, it seems desirable to extend the discussion to a consideration of adsorption at liquid-solid interfaces.

The discussion of this condition, in terms of the present theory, is entirely analogous to the other two types of adsorption, with the single exception that there can be no appreciable alteration of the conditions on the solid side of the interface. Therefore, the adjustment of interfacial conditions must take place exclusively in the liquid phase. In adsorption at liquid-solid interfaces we must appreciate the two possibilities, as at liquid-liquid interfaces—i.e., the energy level in the solid is higher than in the liquid, in which case the more polar constituents of the liquid will be adsorbed; or the energy level in the solid is lower than in the liquid, in which case the less polar constituents will be adsorbed. The two cases are analogous to those just discussed in connection with hydrophobe and hydrophile sols. Two possible examples are polar silica and non-polar carbon.

As to the mechanism of action of dispersed solids in stabilizing emulsions, there seems no reason to alter the previously accepted concept of such action. This has been adequately discussed by Briggs,²⁵ Harkins,²⁶ Gortner,²⁷ Bartell and Osterhoff,²⁸ and many others. The only point which it may be worth while to mention here is to call attention to the very different interfacial conditions between the solid and each liquid, as compared to those between the two liquids. The situation of chief interest in emulsions is when the energy level of the solid plus its adsorbed film is between those of the liquids, as the solid then assumes a position in the interface. The problem, then, is to suitably alter the differential interfacial action so as to cause the removal of the solid from the interface and its dispersion in, for the case of petroleum emulsions, the water phase.

In a further effort to determine the degree of truth of the present theory, as regards adsorption of ions and molecules at the liquid-liquid interface, some experiments are in progress, in which natural emulsions are concentrated by gravity settling, the free oil and water removed and the residual emulsion resolved centrifugally. The characteristics of the several fractions are then determined. This work is still in its early stages, but some partial results can be reported at this time. The results are of interest in that they are analogous to those reported by Holmes for systems of known composition.²⁹

Results on samples of two light-oil emulsions from the Texas Gulf Coast region are shown in Fig. 3, in which data on gravity, surface and interfacial tension, pH of brine and index of refraction are given. The additional tests at present contemplated are dielectric constants, conductivities, interfacial and phase boundary potentials, and magnetic permeabilities. It may be remarked that these samples were chosen for initial tests because it was be-

²⁵ *Ind. Eng. Chem.*, **13**, 1008 (1921).

²⁶ Alexander's "Colloid Chemistry," **1**, 192 (1926).

²⁷ "Outlines of Biochemistry," 154-156 (1929).

²⁸ *Colloid Symposium Monograph*, **5**, 113 (1928).

²⁹ *J. Phys. Chem.*, **29**, 1205 (1925).

lieved that they might show minimum differences between the fractions and would therefore serve to indicate the adequacy of the test methods to show the expected differences. Also, these emulsions lend themselves very well to centrifugal resolution, on a laboratory scale, have no very volatile light ends and are statically quite stable.

Referring to Fig. 3, the columns headed "Free" refer to water and oil recovered by gravity settling; the columns headed "Centrif. Sepd." refer to the tightly emulsified components recovered by centrifugal resolution; while those headed "Chem. Sepd." refer to the oil from the residue of emulsion, which could not be resolved centrifugally and which had to be recovered by

FIG. 3

Property	Sample No. 1		Sample No. 2	
	Free	Centrif. Sepd.	Free	Centrif. Sepd.
Oil—Sp. g. at 60°F.	0.8911	0.8933	0.8956	0.8956
Surface Tension (15 min)	29.1/72.2°	28.9/78.0°	29.3/71.0°	28.9/80.0°
Index of Refrac.	1.4925/70.9°	1.4935/72.0°	1.4913/83.5°	1.4923/83.8°
Brine—Sp. g. at 60°F	1.0728	1.0728		1.0792
pH	6.58	6.75		6.61
Surface Tension (15 min)	64.6/72.0°	59.9/78.0°		60.7/69.0°
Index of Refrac.	1.3502/67.3°	1.3502/69.3°		1.3514/84.2°
Interfacial Tension				
O—W 15 min.	20.9	15.3	18.7	15.6
W—O 15 "	6.0	6.7	16.4	8.5
IT diff. 15 "	+14.9	+8.6	+2.3	+7.1
Temp.	72.2°	78.0°	70.0°	78.8°
Index of Refrac.		Chem. Sepd.		
Oil—Sample No. 1		1.4953/72.9°		
Sample No. 2		1.4959/84.2°		
Chemical Agent		1.4811/74.5°		

All temperatures in Fahrenheit degrees.

combined action of a suitable chemical and the centrifuge. In the latter case, the chemical used had a much lower index of refraction than the oil, so that the values for this fraction are probably somewhat low. The brine from the chemical resolution was not tested because it was known to contain a relatively high proportion of the chemical, which was water-soluble. In both cases, the amount of oil so recovered was too small for anything but refractive index tests. In sample No. 2 no free water settled out, so that but one sample of water, representative of the whole brine, was available. In all the work, every effort was made to prevent evaporation and contamination.

It will be observed that gravities and surface tensions of the oil fractions do not differ appreciably, but that index of refraction data indicate a progressive increase with "tightness" of emulsification. Similarly, the gravities and refractive indices for the brine fractions show no significant differences, while pH increases and surface tension decreases with "tightness" of emulsification. The interfacial tension values given are obtained, for an age of interface of fifteen minutes, by reading from curves of determinations extending over a period of thirty minutes and represent the time when the rate of change has, in most cases, fallen to a low value. Those values indicate a significantly higher

interfacial tension (from oil to water) for the "free" components than for the "emulsified" ones. The data are given exactly as taken, without correction to standard conditions—except in the case of gravities,—as other temperature coefficients have not been determined.

The results seem to indicate an appreciable increase of concentration of polar materials in the tightly emulsified oil and an increase of (in this case) hydroxyl ions in the tightly emulsified brine, both of which observations are concordant with the requirements of the present theory. In this connection, it may be recalled that Dow³⁰ has already shown appreciable differences between the "free" and "emulsified" oil from natural emulsions.

With reference to natural oil-in-water emulsions, of which there are relatively few examples in this country, the principles of the present theory indicate that they should owe their stability primarily to ion adsorption from the external phase, modified by the effect of ionic and molecular adsorption on the inner (oil) side of the interface. The problem of oil-in-water emulsions is, to a great extent, the inverse of the water-in-oil problem.

The effects of temperature, particle size, dissolved or entrained gas, etc., which are often of importance in determining the formation and stability of emulsions, need only be mentioned as factors which alter the concentrations, energy relations, etc., of the primary solutions concerned.

The direct application, of the principles of adsorption here developed, to problems other than those of emulsions is so obvious as to hardly warrant its mention.

It will be remarked that the term "colloid" has not been employed in development of the present theory. There are several reasons for this apparent omission.

First, the term is an extremely indefinite one and leads to no very clear understanding of the mode of operation of "colloids" in stabilizing emulsions. Its use, therefore, would serve only to discourage a more critical search for the specific forces which must be operative.

Second, numerous attempts which have been made to demonstrate the presence of ultramicroscopically visible colloids in crude oils have failed entirely.³¹ In this connection, Gurwitsch³² calls attention to the very doubtful nature of the evidence which has been adduced to prove the presence of colloids in crude oils. Gurwitsch states:³³ "If, however, neglecting the cases of transition, we must define a typical colloidal solution, its most characteristic properties may be said to be; ultramicroscopic inhomogeneity and a capacity for spontaneous alteration of condition even with a constant concentration. . . ." He then proceeds to discuss the evidence under these headings and shows that it fails as proof of the colloidal character of crude oils. Although it is recognized that ultramicroscopic homogeneity is no absolute determination of non-colloidalilty, since the effects observed depend upon refractive index

³⁰ Bur. Mines Bull., No. 250, 85-86 (1926).

³¹ Zeiss cardioid ultra-microscope, with carbon arc, used in this work.

³² "Petroleum Technology," 183-193 (1927), translated by Moore.

³³ "Petroleum Technology," 184 (1927), translated by Moore.

difference, nevertheless the failure of this method was another indication of the desirability of a change in point of view in studying emulsion problems.

Third, even though colloids do stabilize emulsions, they must do so by virtue of the physico-chemical properties of the substances composing the colloidal aggregates.

Fourth, the term colloid, as it is superfluous to remark, designates merely a state of subdivision of matter and has no necessary relation to the properties of that matter, whereas the efficiency of an emulsion-stabilizing material must certainly depend upon its specific molecular properties.

Fifth, the results of extensive research on petroleum emulsions have demonstrated the close relation between emulsion characteristics and ionic and molecular properties of the liquids composing the systems, whereas no systematic relation could be found on the assumption of a colloidal emulsifying agent of unknown composition and properties.

Sixth, it is known that suitable substances, whose particle sizes may range from molecular to macroscopic, are efficient in stabilizing emulsions.

Therefore, it is believed that, even in cases where the so-called emulsifying agent happens to exist within the size range designated as colloidal, the proper mode of attack is to consider the specific molecular properties of the constituents of the system and the changes of properties due to the particular state of aggregation of the several components, as they happen to exist at that time and in that system. The problem then resolves itself into the elements which have been discussed, plus a modification factor based on the state of aggregation. It is also believed, as has already been suggested,³⁴ that a useful application of the term "colloid" would be to the emulsion itself, rather than to some component of the system. In such an application, the dispersed phase, with its surrounding interfacial zone, would be considered the colloid. Such a point of view might bring out more clearly some of the reasons why, for example, an emulsion of extremely small particle size is so much more difficult to resolve than one of larger particle size. In fact, in emulsions of such small particle size that the droplets exhibit Brownian movement, it appears that much of the behavior is quite similar to what is observed in ordinary metal sols.

In view of all these factors, the decision was reached to forget "colloids" entirely and to try to describe emulsion systems in terms of the properties of ions and molecules and their behavior in non-homogeneous systems. The result of this decision is the theory which has been presented. In this connection, attention must be drawn to a publication of Fischer and Harkins,³⁵ relative to the characteristics of liquid-liquid interfacial films. They say, "The work already described proves definitely that: (1) the interfacial film which produces emulsification is not colloidal, and (2) it is not thicker than one molecule of the emulsifying agent, when the emulsifying agent is molecularly dispersed in its solution." Those findings are exactly in accordance with the

³⁴ Gortner: "Outlines of Biochemistry," 10, 11, 33-42 (1929).

³⁵ J. Phys. Chem., 36, 109 (1932).

principles of the new theory and substantiate the wisdom of discarding the term "colloid" in dealing with emulsions.³⁰

As will have been apparent in the course of this presentation, there is perhaps very little which can be considered as original, in the sense that it has never been said before. No claims of a high degree of originality are made, nor is it desired to appear to have employed the ideas of others without giving due credit.

The development of this theory was made necessary by the failure of prior theories consistently and properly to explain the observed facts in connection with petroleum emulsions.

The virtue of the theory, if any, does not necessarily rest upon its originality, but upon the degree to which it permits a relatively simple, consistent and complete explanation of the observed facts connected with the formation, stabilization and resolution of emulsions in general.

Thanks are due and are gratefully rendered to Dr. R. A. Gortner, University of Minnesota, for his helpful and sympathetic discussion and criticism of this theory and to members of the laboratory staff of the Petroleum Rectifying Company, especially Mr. R. L. Belshe, for invaluable assistance in experimental work and theoretical discussion.

Summary

1. A general definition of emulsions has been given and some of the prior emulsion theories have been briefly discussed.
2. The general properties of aqueous and non-aqueous solutions, in terms of ions and molecules, have been defined.
3. The application of known facts and accepted theories of physical chemistry to the problem of emulsification has been discussed.
4. The characteristics of adsorption of ions and molecules at free surfaces have been described.
5. The characteristics of adsorption of ions and molecules at liquid-liquid interfaces have been described.
6. Attention is drawn to the differences in adsorption conditions on the two sides of liquid-liquid interfaces.
7. Explanations of some of the observed characteristics of emulsion systems, which have not been satisfactorily explained by prior theories, are afforded by the present theory.
8. A restatement of the principal problems of emulsification, in the light of the present theory, is given; special reference being made to the particular problems of natural crude oil emulsions.
9. The mechanism of stabilization of an emulsion interface, in accordance with the principles of the new theory, has been described.

³⁰ In connection with Harkins's paper (*J. Phys. Chem.*, **36**, 109 (1932)) it is suggested that the difference between his "expanded" and "condensed" films may be related to their ionic or molecular character.

10. The existence of and necessity for measuring the potentials and interfacial tensions on both sides of liquid-liquid interfaces has been discussed.

11. The measurement of interfacial tensions by the ring method, in which values are determined by pushing from oil to water, as well as, according to the conventional method, by pulling from water to oil, has been described and the possible meaning of the results discussed.

12. The independence of emulsion stability and interfacial potential is discussed.

13. A possible relation between hydrophobe and hydrophile sols and the principles of ionic and molecular adsorption is suggested.

14. The characteristics of adsorption of ions and molecules at solid-liquid interfaces have been described and the effect of solids at emulsion interfaces is discussed.

15. The partial results of separation and determination of the physico-chemical properties of components of some natural emulsions have been presented as evidence of the validity of the new theory.

16. Natural oil-in-water emulsions are briefly discussed.

17. The concept of "emulsifying agents" as "colloids" has been critically discussed and the application of the term "colloid" to the dispersed phase, with its surrounding interfacial zone, is suggested.

*Petroleum Rectifying Company of California,
Long Beach, California,
April, 1932.*

SOME ASPECTS OF BOUNDARY LUBRICATION BY SOAP SOLUTIONS

BY ROBERT C. WILLIAMS

In the course of a study of lubrication as related to the process of drawing wire, some observations have been made which throw light on boundary lubrication in general. Boundary lubrication pertains to conditions accompanying the relative movement of bearing surfaces separated by relatively thin films of lubricant as distinct from thick, fluid film lubrication. High pressures which are localized at points of asperity are concomitant with boundary lubrication.

Wire-drawing is accomplished through the application of lubricants to the wire by various means. The condition of localized high pressures exists and lubricants vary greatly in their ability to facilitate drawing. Lubricants are generally applied in the form of mobile fluids (in which case they act also as coolants), greases or grease-like masses and powders, as for example soap powder. The present report is confined to the study of certain fluid lubricants, involving water as the continuous phase. Little if any fundamental published information exists on lubrication as related to wire drawing.

Experimental

The evaluation of the lubricant solutions was accomplished by drawing wire through a die and measuring the pull on the die or the "die pressure."

Fig. 1 illustrates diagrammatically the method employed. The wire, *A*, was pulled at constant speed through the die, *B*, in the direction indicated. The dynamometer plate, *D*, was in fixed position at the base and was deflected to the right during the drawing process.

The magnitude of the deflection was measured in thousandths of an inch by a dial gauge which was suitably mounted to make contact with the top of the plate, *D*. Various plates represented by *D* were calibrated so that a given deflection represented a pull of so many kilograms. The magnitude of the deflection depended on various factors, such as the size of wire drawn, percent reduction in cross-sectional area effected and so forth. By suitable choice among plates of different deflectability serious displacement of the die bearing from a straight line was avoided as the plate was deflected under load.

It was necessary to keep taut the wire to be drawn and a back pull was therefore provided. The magnitude and uniformity of the back pull influenced the pull on the die to a very marked extent. The wire to be drawn was taken from a spool mounted on a shaft. A pulley which served as a brake drum was mounted on the same shaft and a belt held taut against the pulley by two spring balances provided braking friction. The difference between the readings of the balances when the machine was operating gave the back pull on the wire.

The power for drawing was furnished by a one-quarter horse power A.C. motor which drove speed-reducing gears. A capstan, around which the wire was wrapped two or three times, was mounted on a shaft from the speed reducing gears. The wire was led off from the capstan to a friction driven take-up spool.

The speed of drawing was approximately 30 cm per minute in the experiments reported here. Under most conditions, at any rate, the pull on the die was found to be independent of the speed of drawing between the limits of 30 cm to 3900 cm per minute. This is in accord with the work of F. C. Thompson.¹

It was essential that the wire be clean. This was accomplished through the use of organic solvents—acetone being perhaps the most useful. The development of chattering due to spasmodic seizure of the wire and the die while drawing indicated clean wire and a clean die bearing. Water exerted no lubricating action—chattering not being relieved through its use.

The lubricant solutions were applied by projecting a stream onto the wire and die approach. In the experiments reported here the wire was in contact with the lubricant for not more than two seconds before entering the die bearing as the wire was flooded for a distance of only about 0.5 cm in front of the die bearing. With clean uniform wire and with moderately homogeneous solutions (solutions which did not contain large macroscopic curds or aggregates of dispersed particles), consecutive reading did not vary more than plus or minus five per cent.

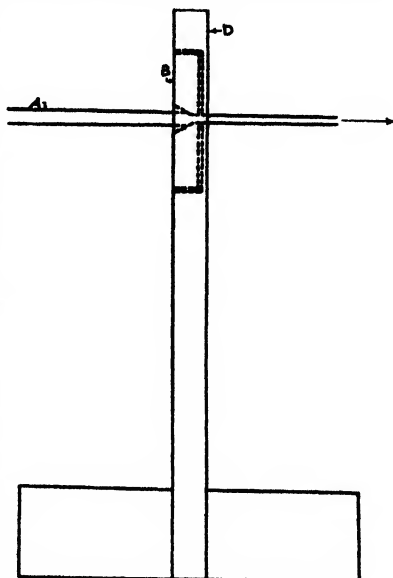


FIG. 1
Wire-Drawing Dynamometer

A Sodium Soap Solution as a Lubricant

Aqueous solutions of sodium or potassium soaps largely constitute or are commonly associated with lubricants for drawing copper wire. A fairly pure, commercial sodium soap of moderately high titre (40.8) was selected for several experiments. In all of the experiments reported here hard drawn copper wire having a diameter of 0.0242 inch was drawn through a 0.0225 inch tungsten carbide die at 30 cm per minute. The back tension on the wire was 1.8 kg. The experiments were carried out at room temperature and no attempt was made to exclude carbon dioxide from the air. Solutions having concentrations higher than 0.0072 *M* were not used as they were too gelatinous at room temperature. Surface tension was measured with the du Noüy tensiometer. pH was measured colorimetrically using Hellige Klett equip-

¹ Sixth Sorby Lecture 10/10/30 pp. 1 to 24, Department of Applied Science, St. George's Square, Sheffield, Eng.

ment. Boiled-out distilled water was used in making up the solutions. The results obtained with solutions of this soap are presented in Tables I and II.

TABLE I
The Relation of Concentration to the Lubricating Effectiveness of a Sodium Soap

Mols per Liter	Percent Reduction in Pull on Die compared with Water* (Reduction means Increased Lubricating Efficiency)	pH of solution	Surface Tension of Solution in Dynes/cm.
0.0072	22	9.4	27.1
0.0036	22	9.4	26.7
0.0018	15	9.6	26.9
0.00082	11	9.3	26.9†
0.00041	11	8.7	29.7
0.000205	6	8.3	32.6

* With water seizure was experienced the pull on the die then being 9.1 kg. This held for all experiments reported here.

† The first reading at this point was 29.3, some time being necessary to reach the steady value of 26.9.

TABLE II
The Relation of pH to the Lubricating Effectiveness of a 0.0033M Solution of a Sodium Soap

pH of Solution*	Surface Tension of Solution in Dynes/cm.	Percent Reduction in Pull on Die compared with water
7.3	30.7	25†
8.6	27.1	23
9.5	26.9	22
11.7	34.7	19
12.1	34.7	15
12.4	34.9	0
12.7	34.7	0

* HCl was added to lower the normal pH, i.e. 9.5, and NaOH was added to obtain the higher values.

† Small particles of fatty acid or acid soap at pH 7.3 apparently made both the surface tension and die pull readings erratic.

As the concentration of the solution was decreased the effectiveness of the solution as a lubricant diminished rather sharply at a concentration neighboring that which first exhibited a definite increase in surface tension. This effect is presumed to be due to the incomplete formation of a film of lubricating material on the wire—the conditions supposedly being analogous to incomplete film formation at the air-water interface as indicated by the surface tension measurements. Had surface tension been measured by a dynamic method it is quite possible that the upward break in surface tension would have occurred at the same concentration as did the downward break in effectiveness of lubrication.

The pH data indicate the hydrolysis increased so rapidly with decreasing concentration that a maximum was reached. This increase in hydrolysis with dilution is in harmony with the work by McBain.²

A consideration of the constitution and behavior of soap solutions leads to an explanation of the rather surprising results given in Table II. In dilute soap solution the pronounced hydrolysis gives rise to free alkali, and accounts for the pH, fatty acid and acid soap. Addition of alkali repressed the hydrolysis, caused the disappearance of uncombined fatty acid and acid soap and decreased the lubricating effectiveness of the solution to zero. The equilibria in a soap solution system which are disturbed by the addition of alkali are given in Fig. 2. It was found that the addition of sodium chloride which, of course

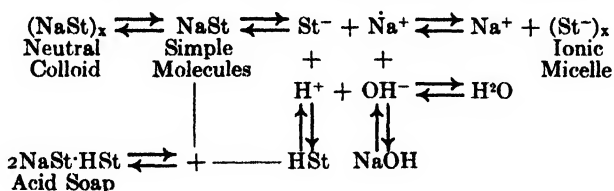


FIG. 2

Soap Solution Equilibrium Diagram (Sodium Stearate).

yields the common ion, sodium, exerted no such effect on lubrication at equivalent concentrations as did sodium hydroxide. Since the effect of the sodium ion in increasing the colloidal constituents was not responsible for the decreased lubrication it is apparent that fatty acid or acid soap was responsible for the lubrication by the soap solution.

A Fat Emulsion as a Lubricant

Particularly striking were the results with an emulsion of tallow in a sodium soap solution which are presented in Tables III and IV.

TABLE III

The Relation of Concentration to the Lubricating Effectiveness
of a Tallow-Sodium Soap-Water Emulsion

Concentration of Emulsion*	Percent Reduction in Pull on Die compared with Water	pH	Surface Tension of Solution in Dynes/cm.
2%	21	9.2	29.7
1%	21	9.4	31.1
0.5%	19	9.3	30.7
0.2%	19	9.2	31.4
0.1%	19	9.0	34.0
0.05%	15	8.5	37.3

* A concentrated emulsion was used which contained 60% tallow (free fatty acid content 0.5%), 20% sodium soap and 20% water. This was used in making the dilute emulsions, for example, 2 parts of the concentrate were used with 98 parts of water to make a "2% emulsion."

² Bogue's: "Colloidal Behavior," 1, 410 (1924). (Good summary and bibliography.)

TABLE IV

The Relation of pH to the Lubricating Effectiveness of
a 2% Tallow-Sodium Soap-Water Emulsion

pH of Solution	Surface Tension of Solution in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
6.8	27.8	25
9.2	29.7	21
11.7	33.2	17
12.1	35.4	16
12.4	35.4	9
12.7	35.8	0

It is noteworthy that the incorporation of tallow in the soap solution did not alter the trend of the results. Under the experimental conditions the relatively large proportion of tallow in the solution apparently played a comparatively minor rôle in the lubrication at the wire and die interface. Fatty acid or acid soap was apparently the factor upon which lubrication depended in this case also.

Triglycerides which are supposedly free from fatty acid possess definite lubricating value though they are markedly inferior to fatty acids. Wells and Southcombe,³ in their important investigations, found that it was necessary to add to mineral oil 60 to 80% of rapeseed oil, which had been freed from fatty acids, to obtain the same degree of lubrication that was obtained by the addition of 1 to 2% rapeseed oil fatty acids.

The triglycerides in tallow, which should also possess lubricating value, did not apparently come into contact with the wire at high pH values at least.

An Ammonium Soap as a Lubricant

Tests similar to the above were carried out using solutions of ammonium linoleate. The results are presented in Tables V and VI.

TABLE V

The Relation of Concentration to the Lubricating Effectiveness
of Ammonium Linoleate

Concentration in Mols* per Liter	pH of Solution	Surface Tension in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
0.0714	8.8	26.9	20
0.0357	8.8	27.4	22
0.01785	8.7	27.6	26
0.00714	8.6	27.6	28
0.00357	8.6	27.6	26
0.00179	8.4	29.2	23

* Given on basis of fatty acid since the ammonia volatilized somewhat.

³ Chemistry and Industry, 39, 51 T (1920).

TABLE VI

The Relation of pH to the Lubricity of a 0.00714 M Solution of Ammonium Linoleate

pH of Solution*	Surface Tension in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
8.6	27.6	28
9.3	27.4	25
9.5	27.6	22
9.6	27.6	19
9.8	27.4	19
10.0†	27.6	19

* Ammonia was added to increase the pH.

† This solution was not at all turbid.

It is well known that ammonium soaps hydrolyze to a much greater degree than do sodium or potassium soaps except in the very dilute range where both hydrolyze almost completely. Ammonium hydroxide, being a weak base, produced a comparatively low degree of alkalinity in the solutions. As the concentration of the soap was decreased the alkalinity remained remarkably constant.

It is believed that the physical state (degree of peptization) of the fatty acid particles is a factor which, in part, accounts for the maximum lubricating effectiveness of the 0.00714 M solution. Subsequent work on emulsions having particles of different ranges in size has given weight to this belief. The experiments involving the deliberate variation in pH are in harmony with the preceeding analogous experiments with the other solutions. When the pH of the ammonium linoleate solution was markedly increased by the addition of sodium hydroxide the effect on lubrication was the same as previously.

The well-known work of Sir W. B. Hardy and his collaborators⁴ shows the importance of fatty acids and other long chain polar compounds in lubrication. Although soap is an example of this type of compound the evidence presented here showed that soap solutions free from fatty acid do not possess lubricating properties. The X-ray studies by Trillat⁵ indicate that fatty acid molecules are approximately perpendicularly oriented at the surfaces of solids with the COOH group turned towards the solid. With certain metals the nature of the spectrum at the metallic surface was such that it could be distinguished from the fatty acid spectrum. This difference was attributed to a combination of the fatty acid with the metal. It seems reasonable that in accordance with Trillat's experiments, fatty acids would be much more readily adsorbed by metals than a soap, such as a sodium soap, which is itself the result of the combination of a fatty acid and a metal.

⁴ Alexander's "Colloid Chemistry," 1, Chap. 13 (1926). Chapter including bibliography by Hardy.

⁵ Compt. rend., 180, 1838 (1925); Metallwirtschaft, 7, 101 (1928); 9, 1023 (1930).

Summary

An apparatus has been devised for the study of lubricants and lubrication as related to wire drawing in particular.

The lubricating effectiveness of sodium and ammonium soap solutions was due to the products of hydrolysis, fatty acid or acid soap.

When hydrolysis was sufficiently repressed lubrication by soap solutions was entirely lacking.

When fat (tallow) was emulsified in a soap solution, lubrication was not appreciably affected at low or high pH values.

No parallelism existed between the lubricating effectiveness and the surface tension of the solutions when the pH was varied. However, as the concentration of a given solution was decreased to a point neighboring that at which the lubricating effectiveness diminished rather sharply the surface tension increased.

There was an indication that the degree of peptization of the fatty acid or acid soap was a factor in lubrication by soap solutions.

Acknowledgment

The writer wishes to express his thanks to the Ironsides Co. and to the Battelle Memorial Institute for permission to publish this work.

The writer is particularly indebted to Drs. H. W. Russell and O. E. Harder of the Institute staff for their aid and encouragement.

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ADHESION TENSION

A Receding Contact Angle, Pressure of Displacement Method

BY F. E. BARTELL AND CHARLES E. WHITNEY

During the past five years a number of investigations have been reported in which adhesion tension values of certain solid-liquid systems have been obtained. In nearly all of these investigations the original pressure of displacement method of Bartell and Osterhof¹ was used. With this method finely divided solid material is compressed into a membrane. Liquid is brought into contact with this membrane and the pressure is measured which is just sufficient to prevent movement of liquid through its pores. At the very beginning of the experiment liquid is allowed to advance, but very shortly thereafter further advance is prevented by gradually building up an opposing pressure. Advance of liquid is detected by noting movement of liquid in the indicator tube attached to the low pressure side of the system.

At the time of the original pressure of displacement work it was assumed that one and only one definite equilibrium contact angle was possible for any given solid-liquid-air (or solid-liquid-liquid) system. The existence of advancing and of receding angles was well known, but it was assumed, at least by us, that either an advancing or a receding angle would, within a short time, so adjust itself as to give finally a definite equilibrium angle which would be the same whether approached from the advancing or the receding angle. We have since obtained good evidence that advancing angles and receding angles may each exist as definite, but different, equilibrium angles. A careful consideration of the precise method used in the earlier work led us to believe that the periodic increases in pressure imposed upon the system gave a final pressure which in nearly every case was ascribable to the effect of the receding equilibrium angle; we could not be absolutely certain, however, that this was actually the case.

Somewhat over two years ago an attempt was made in our laboratory to construct an apparatus with which a liquid system advancing by capillarity within the pores of the membrane would automatically build up a pressure which would reach a maximum value and would then serve as a measure of the balancing or equilibrium pressure. Throughout the operation of this method the contact angle would at all times be of the advancing type. At present we need state only that much difficulty was encountered in our attempts to obtain reproducible values. The details of this work will be presented in another paper. A still later investigation on contact angles, in our laboratory (unpublished), has shown that receding angles are more easily reproducible than are advancing angles. In view of the above findings it was decided to carry

¹ Bartell and Osterhof: Colloid Symposium Monograph, 5, 113 (1927); Ind. Eng. Chem., 19, 1277 (1927); Z. physik. Chem., 130, 715 (1927); J. Phys. Chem., 34, 1399 (1930).

out an investigation in which the displacement pressure apparatus would be so operated that receding contact angle measurements would of certainty be obtained. In carrying out this plan the membrane pores were first completely filled with liquid and then the minimum pressure required to force back the liquid column was determined.

Experimental

Apparatus.

Displacement Cell. An assembled cell and its parts are shown diagrammatically in Fig. 1. The cells were similar in construction to those used by Bartell and Osterhof.¹ They were shorter, the chamber being about 23 mm in length; one end was solid except for a small outlet to which a connection was made with a manometer. A glass capillary indicator tube was attached to the other end of the cell.

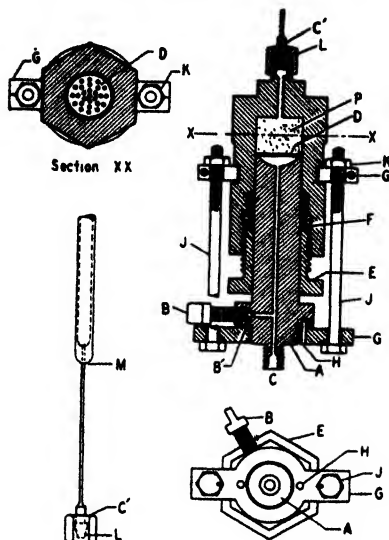


FIG. 1

Assembly and Details of Cell

Manometer. The manometer was of the simple U-tube type with an auxiliary or third arm. One arm of the manometer was of 7 mm glass tubing. This was sealed to a ground-glass joint by means of which connection was made with the cell. The second arm was a capillary tube in which the mercury level was regulated and observed. The third or auxiliary arm was joined to the bottom of the U-tube next to the capillary arm. It was provided with a stopcock with which it could be shut off from the rest of the manometer.

The main purpose of this third arm was to serve as a reservoir making possible a gradual lowering of the mercury in the capillary tube. At the lowest part of the manometer was a capillary outlet consisting of a stopcock and a drawn-out tip. This outlet was for the purpose of removing mercury slowly in order to bring about a gradual decrease of pressure within the manometer system. The connection from the manometer to the cell consisted of a ground glass joint above which was a 3-way stopcock. Above the stopcock was a small bulb and beyond this was a copper tube attached to a small union C, C', L (Fig. 1) with which final connection was made.

Packing Apparatus. A method was developed for packing a powder into the form of a membrane so that a given amount of either wet or dry powder might be used and give essentially the same volumes.² The packing or tamping machine used for packing the powder in the the cell was developed by Bartell and Jennings.² Briefly, it consisted of a packing plunger 2.5 kilograms in weight which was raised by turning a crank and caused to fall on

² Bartell and Jennings: unpublished.

the powder in the cell. A suitable device held the cell in position and kept the plunger in alignment during its fall. The apparatus was adjusted so as to allow the plunger to fall a distance of 85 mm.

Thermostat. The experimental determinations in this work were all carried out in an air thermostat at 25°C. The temperature was controlled to within 0.1°C.

Materials.

Silica. The only solid used in this work was silica, a ground Ottawa sand of fairly high purity. It was twice treated with boiling 1:1 HCl, then with hot water and filtered. The silica was then washed with boiling water about twenty times. It was dried in an oven at 100°C and muffled at red heat for about 2 hours. It was graded by sieving, about three-fourths of it passed thru at 350 mesh, the remainder was discarded. This screened powder contained not only particles which would just pass thru the sieve but also much very fine powder which if shaken up with water would not settle out for several days. Such variation of particle size was not desirable as the pore size of the compressed membranes formed with it would not be uniform. In order to obtain a smaller range of particle size, the silica which had passed thru the 350 mesh sieve was stirred up in a large crock of distilled water and was allowed to settle for 30 minutes. The suspension which had not settled out was siphoned off and the settled powder was carried thru this sedimentation process again. The settled powder was then dried and again muffled at red heat for 2 hours.

A test was made to determine whether the surface tension of liquids would be altered by standing in contact with this silica. Some of it was shaken with pure water. After removal of the silica by centrifuging, there was no change in the surface tension of the water. This indicated absence of water soluble impurities in the silica.

Liquids. All of the liquids used in this work were of good grade, though not of "highest purity." Determinations of the surface tensions of the liquids gave values which were in good agreement with accepted values.

Experimental Procedure.

Packing. The cell was placed in the packing apparatus. A small circular piece of linen cloth was placed in the bottom of the cell. This was to prevent silica being forced or blown out of the cell by the fall of the packing plunger upon the silica. Approximately 1 gram of silica was placed in the cell and a piece of cloth inserted on top of it. The silica was then subjected to 50 impacts of the plunger. About 6 one-gram increments of silica were used for the preparation of the membrane. The top cloth was removed before each addition of silica and then replaced for each packing operation.

Measurement of Pressure and Determination of Pore Size. After a cell had been packed it was assembled as shown in the diagram in Fig. 2. The liquid (a liquid which forms zero contact angle with the solid) was then drawn into the cell so as to wet the membrane completely. The tube connecting to the

manometer was filled with liquid as far as the stopcock. It was then joined to the cell by means of the union. The cell was set up as shown in Fig. 1, and the connection to the manometer made by means of the ground-glass joint. The mercury level in the manometer was raised until mercury filled the 3-way stopcock. This stopcock was turned so as to make direct connection between the mercury and the liquid which extended into the cell. The mercury and liquid interface was then raised by loosening the valve, (*B* of Fig. 2), and raising the mercury level in the manometer. In this way the level of this interface was raised into the small bulb. Correction was made for the capillary depression of mercury in the capillary as well as for the liquid column which extended from the mercury level in the bulb to the cell. Since the final "negative" pressure was measured by the difference in the levels of the mercury in the bulb and in the capillary these corrections could be made simultaneously by noting the difference in levels of the two mercury menisci when the valve, *B*, was open, or in other words when both columns were open to the air. After making this reading the valve was tightly closed. The indicator tube was then connected to the other end of the cell. A column of colored liquid was placed in this indicator tube to show when movement of the liquid in the cell occurred. The cell and manometer thus assembled were ready for the determination of the displacement pressure.

With the auxiliary arm of the manometer in direct connection, the outlet tube at the bottom of the manometer was partially opened. This was adjusted so as to give a very gradual lowering of the mercury in the capillary and auxiliary tubes. The pressure differential was thus increased slowly until the liquid in the indicator tube began to move. The pressure was then allowed to remain constant for a few minutes until the indicator liquid again became stationary. This procedure was repeated until the liquid showed a continuous movement in the cell towards the manometer. The success of the measurement is dependent upon a sufficiently slow and careful increase in the pressure differential. The pressure differential (*i.e.*, "negative pressure") which caused the continuous movement of the liquid was regarded as the equilibrium displacement pressure corresponding to the receding contact angle. Strictly speaking, this pressure was that required to draw air into the liquid-filled pores rather than the pressure required to prevent the displacement of air from the pores by the liquid. The small movements of the liquid which occurred before the maximum or equilibrium pressure was reached were attributed to displacement of the liquid from the linen disc at the end of the membrane and also to variations in the pore radii of the membrane. A pressure less than the equilibrium pressure was sufficient to initiate movement in a few large pores and this movement continued until smaller pores were reached. The movement of the liquid became continuous when the maximum pressure for the effective pore radii was reached, for at this pressure the liquid was probably moving in practically all of the larger pores.

A similar method was tried out in which the pressure was positive, *i.e.*, pressure was built up by increasing the mercury head on the high pressure side of the system. The pressure was measured which was just sufficient to drive

liquid through the membrane. The results thus obtained give good agreement with those reported herein. The "pull method" is limited in use to systems in which the displacing pressure is not greater than atmospheric pressure.

From the maximum (equilibrium) pressure values obtained the pore size was calculated by the equation,

$$r = \frac{2S}{hdg} = \frac{2S}{Pg}^*$$

Data obtained in measurement of pore size of the silica membranes used are given in Table I.

TABLE I

Determination of Pore Size of Compressed Silica Powder Membranes

System	P grams/cm ²	S dynes/cm	r × 10 ⁻⁴ cm
Water—Air—Silica	469	72.08*	3.13
Water—Benzene—Silica	229	34.76**	3.10
Water—Nitrobenzene—Silica	166	25.32**	3.10
Average			3.11

* Surface Tension

** Interfacial Tension

It might be mentioned that Bechhold,³ and Bigelow and Bartell,⁴ as well as others have measured pore radii of porous membranes by determining the pressure required to force liquid out of the pores. In principle that method and this one are essentially the same.

We found it possible to measure pore size by means of liquid-liquid as well as liquid-air systems. Bartell and Greager⁵ measured interfacial tensions by a displacement pressure method in a porous membrane of calcium fluoride. Bechhold and Schnurmann⁶ have also used liquid-liquid systems to measure pore size of porous membranes and found that the values agree closely with those obtained with liquid-air systems. In carrying out similar measurements in this work the compressed membrane was first wetted completely with water and the water-organic liquid interface was then drawn into the pores. The pressure required to prevent displacement of the organic liquid by the water was then measured.

Determination of Adhesion Tension of Contact Angle Forming Liquids. The determination of the adhesion tension of liquids, which in contact with air

* The symbols used in this paper are the same as those used in recent publications from this laboratory, namely: S_1 = Surface tension or free surface energy of solid phase; S_2 = Surface tension or free surface energy of liquid phase; S_3 = Surface tension or free surface energy of water.

A combination of subscripts refers to interfacial tension values as S_{12} = interfacial tension of organic liquid against water, S_{13} = interfacial tension of organic liquid against solid, etc. θ represents the angle of contact, P represents the displacement pressure, and g represents the gravitational constant.

³ Z. physik. Chem., **64**, 328 (1908).

⁴ J. Am. Chem. Soc., **31**, 1194 (1909).

⁵ Unpublished work completed in May, 1929.

⁶ Z. physik. Chem., **142**, 1-24 (1929).

form contact angles with silica, was readily carried out by measuring the contact angle formed in each case. The membrane was completely wetted with the contact angle forming liquid, the cell and manometer set up, and the pressure differential increased until the liquid started to be pulled back through the cell. (The pressure at which this occurred was lower than that corresponding to the force of surface tension of the liquid and the extent of this lowering is directly related to the magnitude of the receding contact angle.) The auxiliary arm of the manometer was then shut off from the capillary by means of the topcock provided for that purpose, the mercury in the capillary began to rise as the liquid within the membrane receded. After a period of time this movement ceased and the liquid became stationary as did the mercury column in the manometer. The pressure remained constant at that point for several hours. This pressure value was quite reproducible and was considered to be representative of the receding equilibrium contact angle. The contact angle was calculated by use of the equation,

$$\cos \theta = rPg/2S. \quad (2)$$

The adhesion tension, A_{12} , of the contact angle forming liquid was calculated by use of the equation,

$$A_{12} = S_2 \cos \theta, \quad (3)$$

or from the more general equation,

$$A_{12} = S_2 K,$$

in which K may be considered as the adhesion constant which may have a value greater than unity. Adhesion tension values were determined for five liquids which form contact angles against silica and are to be found in Table II.

TABLE II
Adhesion Tension Determinations of Contact Angle-Liquids
Organic Liquid—Air-Silica

	$r = 3.11 \times 10^{-4} \text{cm}$					
	P	θ	$\cos \theta$	S_2	A_{12}	
	grams/cm ²			dynes/cm	dynes/cm	
Acetylene tetrabromide	281	29°25'	0.874	49.07	42.8	
Alpha Brom-naphthalene	260	25°43'	0.901	44.00	39.6	
Alpha Chlor-naphthalene	256	18°44'	0.947	41.20	39.0	
Bromoform	245	23°56'	0.914	40.93	37.4	
Iodobenzene	243	18°00'	0.951	39.10	37.2	

Determination of the Adhesion Tension of Water. The adhesion tension of water against silica was determined by the measurement of the contact angles formed by liquid-liquid-solid systems. The organic liquid used was one which forms a contact angle with silica and whose adhesion tension against silica had been measured as previously described. The determination of the interfacial contact angle formed by the water-organic liquid interface against silica required a slightly different procedure from that used for the determination of

the solid-liquid-air angles previously described. The compressed powder membrane was wetted completely with the contact angle forming liquid and then a small increment of silica wetted with water was packed on top of the silica wetted with the organic liquid. The cell was then assembled and set up as in previous measurements. The pressure differential was increased slowly within the system until movement of the liquids in the cell ceased. When this occurred the auxiliary arm of the manometer was shut off as in the previous determination and the system allowed to attain equilibrium. This was assumed to have been reached when the pressure differential was so great that there was no more displacement of the organic liquid by the water. The interfacial contact angle was then calculated by means of the equation,

$$\cos \theta_{23} = rPg/2S_{23}. \quad (4)$$

Since the adhesion tension, A_{12} , of the contact angle forming liquid was known and the value of the contact angle of the interface likewise known, the adhesion tension, A_{13} , of water against silica was calculated by means of the equation,

$$A_{13} = A_{12} + S_{23} \cos \theta_{23}. \quad (5)$$

Five separate determinations of the adhesion tension of water against silica were carried out using water with each of the five contact angle forming liquids previously mentioned. These results are to be found in Table III.

Determination of the Adhesion Tension of Zero Contact Angle Liquids. The determination of the adhesion tension of organic liquids which form a zero contact angle with silica was carried out by the measurement of interfacial contact angles. In this case, however, the adhesion tension of water was known and the adhesion tension, A_{12} , of these organic liquids was calculated by equation (5). The procedure used in obtaining the interfacial contact angles was practically the same as in the last case mentioned, the only difference being the use of organic liquids which form zero contact angles with silica in place of the ones which form finite angles. Thirteen such organic liquids were used. Eight of them had been used in previous investigations but were used in this work so that the results might be compared with those obtained by other methods. The results are given in Table IV.

TABLE III

Adhesion Tension Determinations of Water against Silica By Measurement of Interfacial Contact Angles

(Water—Organic Liquid—Silica)

	P grams/cm ²	θ_{23}	$\cos \theta_{23}$	S_{23} dynes/cm	A_{12} dynes/cm
Acetylene tetrabromide	221	28° 29'	0.879	38.32	76.4
Alpha Brom-naphthalene	242	27° 15'	0.889	41.57	76.6
Alpha Chor-naphthalene	245	21° 52'	0.928	40.24	76.3
Bromoform	261	9° 15'	0.987	40.35	77.2
Iodobenzene	260	16° 3'	0.961	41.34	76.9
Average					76.7

TABLE IV

Adhesion Tension Determinations of Zero Contact Angle Liquids against Silica

Water $A_{12} = 76.7$ dynes/cm. $K = 1.07$

Water—Organic Liquid—Silica

 $r = 3.11 \times 10^{-4}$ cm

	P grams/cm ²	θ_{23}	$\cos \theta_{23}$	S_{23} dynes/cm	S_2 dynes/cm	A_{12} dynes/cm	K^*
Butyl acetate	79.8	22°20'	0.925	13.2	24.1	64.5	2.68
Nitrobenzene	125	41°25'	0.750	25.3	43.3	57.7	1.33
Chloroform	192	22°11'	0.926	31.6	26.5	47.4	1.79
Benzene	215	19°16'	0.944	34.7	28.2	44.1	1.56
Toluene	221	21°57'	0.928	36.5	28.1	43.2	1.54
Carbon disulfide	226	44°16'	0.716	48.1	31.2	42.3	1.34
Ethyl benzene	233	22°20'	0.925	38.4	28.5	41.2	1.45
Chlorobenzene	240	15°36'	0.963	37.9	32.6	40.2	1.23
Propyl benzene	241	23°13'	0.919	40.0	28.6	40.0	1.40
Brombenzene	245	19°20'	0.944	39.6	35.9	39.3	1.09
Butyl benzene	249	24°3'	0.913	41.6	28.8	38.7	1.34
Carbon tetrachloride	265	24°46'	0.908	44.5	26.1	36.3	1.39
Hexane (synthetic)	333	4°35'	0.997	51.0	18.2	25.9	1.42

* $K = A_{12}/S_2$ (or $A_{12} = KS_2$)

Discussion of Results

In Tables V and VI are given adhesion tension values for a series of liquids against silica obtained by the original pressure of displacement method,¹ values obtained by the single transparent capillary tube method,⁷ and values obtained by the present "receding contact angle pressure of displacement" or so-called "pull" method.

Reasonably good agreement is noted throughout for the adhesion tension values of contact angle forming liquids listed in Table V. The adhesion tension values obtained for water against silica show good agreement for the single capillary method and the "pull" method, the average values being 75.8 and 76.7 dynes/cm, respectively. The corresponding value obtained with the original pressure of displacement method was 81.5 or about 6 dynes/cm higher. This difference in values can be attributed to one of two things, either (1) the free surface energy of the silica (tripoli) used in the original investigation was different from that of the fused quartz and the sand of the other investigation, or (2) the higher value for the adhesion tension of water obtained in the original investigation was due to experimental errors in that work. The value obtained was dependent upon results of work with one contact angle forming liquid only, namely, alpha bromnaphthalene. An error in the determination of the interfacial contact angle of alpha bromnaphthalene against water would account for the difference in values obtained. This work

⁷ Bartell and Merrill: J. Phys. Chem., **36**, 1178 (1932).

TABLE V

Comparison of Adhesion Tension Values obtained by Different Methods
Contact Angle Forming Liquids against Silica

	Original Pressure Method A_{12}	Single Capillary Method A_{12}	Present Method A_{12}
Acetylene tetrabromide		43.3	42.8
Alpha Brom-naphthalene	41.1	41.1	39.6
Alpha Chlor-naphthalene		39.8	39.0
Bromoform		37.3	37.4
Iodobenzene		38.2	37.2

Water against Silica

(Water—Organic Liquid—Silica System)

	A_{13}	A_{13}	A_{13}
Acetylene tetrabromide		76.3	76.4
Alpha Brom-naphthalene	81.5	75.9	76.6
Alpha Chlor-naphthalene		76.2	76.3
Bromoform		75.3	77.2
Iodobenzene		75.5	76.9
Average	81.5	75.8+	76.7

has been rechecked and we have no good evidence of any error in the original work. It seems then that the most logical conclusion is that the original silica used (tripoli) possesses surface properties different from those of fused quartz and of sand.

In Table VI are given adhesion tension values obtained by each of the three methods for a series of organic liquids against silica. Again it is noted that good agreement was obtained with the single capillary method and the

TABLE VI

Comparison of Adhesion Tension Values obtained by Different Methods

Zero Contact Angle Liquids against Silica

Water—Organic Liquid—Silica

	Previous Pressure Method	Single Capillary Method	Present Method
Butyl acetate	72.1	66.6	64.5
Nitrobenzene	61.4	57.3	57.7
Chloroform	58.7	45.4	47.4
Benzene	51.2	46.5	44.1
Toluene	53.4	46.5	43.2
Carbon disulfide	43.2	40.5	42.3
Carbon tetrachloride	39.5	35.6	36.3
Hexane (synthetic)		29.9	25.9

"pull" method while the values obtained with the original method are uniformly higher. These higher values are to be expected if one considers that the values obtained for each of these liquids is dependent upon the value for water used in the calculation.

Were the value of 76 to be accepted as the adhesion tension value for water against tripoli (as it appears to be for the other forms of silica), then the adhesion tension values for the other liquids against it would be practically the same as obtained for them against fused quartz and sand. As above stated we have no good reason to believe that the earlier work is seriously in error, so we shall conclude for the present that the surface properties of the different forms of silica are different. This latter view appears to be justified from more recent work in this laboratory which is as yet unpublished in which it has been shown conclusively that the surface properties of surfaces such as of silica are dependent upon the precise treatment to which they are subjected.

Work of Adhesion. Water vs. Solid Surfaces against a Series of Organic Liquids. It was found by Bartell and Hershberger⁸ that decreases in free surface energies which occur when a polar solid and each of a series of liquids are brought together are in the same direction and of the same relative magnitude as the decreases which occur when the same series of liquids are brought into contact with water. Harkins and Dahlstrom⁹ have observed that: "the energy relation at the interface between solid oxides and organic liquids are similar to those between water and the same organic liquids."

The data obtained in the present work tends to substantiate these generalizations and has shown further a definite relationship between the work of adhesion of a series of organic liquids for silica and for water. The work of adhesion, W_a , represents the change in energy (ΔF) which occurs when a given phase, as a solid, comes in contact with a liquid, i.e.,

$$\Delta F = W_a = S_1 + S_2 - S_{12}. \quad (6)$$

Similarly when an organic liquid surface and a water surface come together the free surface energy relations may be expressed as follows:

$$\Delta F' = W_a' = S_3 + S_2 - S_{23}. \quad (7)$$

The free surface energies of a solid-air or of a solid-liquid interface are not determinable but the decrease in free surface energy which occurs when a solid-air interface is replaced by a solid-liquid interface is represented by the adhesion tension of the liquid against the solid. It is therefore permissible to use the following equation:

$$\Delta F = W_a = A_{12} + S_2. \quad (8)$$

By the substitution of appropriate data in equation (8), the work of adhesion of an organic liquid against silica can be calculated. Such calculations were made for all the organic liquids used in this work and the results are given in Table VII. Similarly from equation (7), the work of adhesion of these same

⁸ Ind. Eng. Chem., 22, 1304 (1930).

⁹ Ind. Eng. Chem., 22, 897 (1930).

organic liquids against water was calculated. Also the ratios of the work of adhesion of the organic liquids against silica to the work of adhesion of the same liquids against water were calculated and are given in the last column of Table VII.

TABLE VII

Comparison of the Work of Adhesion of Organic Liquids against Silica
and of the Same Liquids against Water

Organic Liquid against Silica	Organic Liquid against Water						
	$W_a = S_1 - S_{12} + S_2$ or $W_a = A_{12} + S_2$						
	A_{12} ergs	S_2 ergs	W_a ergs/cm ²	S_{23} ergs	$S_2 - S_{23}$ ergs	W_a' ergs/cm ²	W_a/W_a'
Nitrobenzene	57.7	43.3	101.0	25.3	46.8	90.1	1.12
Acetylene tetrabromide	42.8	49.1	91.9	38.3	33.8	82.9	1.11
Butyl acetate	64.5	24.1	88.6	13.2	58.9	83.0	1.07
Alpha Brom-naphthalene	39.6	44.0	83.6	41.6	30.5	74.5	1.12
Alpha Chlor-naphthalene	39.0	41.2	80.2	40.2	31.9	73.1	1.10
Bromoform	37.4	40.9	78.3	40.4	31.7	72.6	1.08
Iodobenzene	37.2	39.1	76.3	41.3	30.8	69.9	1.09
Brombenzene	39.3	35.9	75.2	39.6	32.5	68.4	1.10
Chloroform	47.4	26.5	73.9	31.6	40.5	67.0	1.10
Carbon disulfide	42.3	31.3	73.9	48.1	24.0	55.6	1.33
Chlorbenzene	40.2	32.6	72.8	37.9	34.2	66.8	1.09
Benzene	44.1	28.2	72.3	34.6	37.5	65.7	1.10
Toluene	43.2	28.1	71.3	36.1	36.0	64.1	1.11
Ethyl benzene	41.2	28.5	69.7	38.4	33.7	62.2	1.12
Propyl benzene	40.0	28.6	68.6	40.0	32.1	60.7	1.13
Butyl benzene	38.7	28.8	67.5	41.6	30.5	59.3	1.14
Carbon tetrachloride	36.3	26.1	62.4	44.5	27.6	53.7	1.16
Hexane	25.9	18.2	44.1	51.0	21.1	39.3	1.12

From this table it can be seen that the relative order of decrease in the values of the work of adhesion from liquid to liquid in a series of organic liquids is the same in the case of both silica and water. From the obtained ratio, W_a/W_a' , it is to be noted that the values representing free surface energy changes must be of the same order for silica and water since the ratio obtained is quite close to unity.

Conclusions which can be drawn from this investigation are that the receding contact angle pressure of displacement method is comparatively rapid, the results are duplicable and the adhesion tension values calculated from the data obtained with this method are reliable adhesion tension values for the systems in question.

Summary

1. A pressure of displacement method was developed for the measurement of receding contact angles formed within the pores of a membrane of compressed powder. The time required to reach a final characteristic pressure value was much shorter than with methods previously used.
2. The adhesion tension values for water against silica calculated from data obtained by this method agree closely with values obtained by the single capillary method. They are about 6 dynes/cm lower than the values obtained by the previous pressure of displacement method.
3. The adhesion tension values and the contact angle values obtained by this method for liquids which form contact angles with silica are in close agreement with values obtained by the single capillary method.
4. The adhesion tension values of various organic liquids (including zero contact angle forming liquids) against silica determined in this work agree closely with those obtained with the single capillary method and are consistent with those obtained in previous displacement pressure work.
5. The adhesion tension values against silica of several organic liquids not previously used have been determined.
6. Further evidence has been obtained that the free surface energy changes which occur when given organic liquids come in contact with polar solids are of the same relative order as the corresponding energy changes which occur when these same liquids come in contact with water. The ratio of the work of adhesion of an organic liquid with silica, W_a , to the work of adhesion of the organic liquid with water, W_a' , is a constant whose value is close to unity (ave. value = 1.1+).

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ALUMINA LAKES*

BY WILDER D. BANCROFT AND ESTHER COE FARNHAM

Reinmuth and Gordon¹ have prepared what they claim to be the aluminum salt of Orange II acid by several methods. Since many alumina lakes are adsorption complexes and not definite chemical compounds, it seemed desirable to make a phase rule study of the alumina lakes of alizarin and Orange II. The Orange II was furnished us through the courtesy of the duPont Company. The free acid was prepared by the method of Sisley.² Orange II acid is soluble enough in water to be used that way; but alizarinic acid must be used in alcoholic solution.

Powdered alumina from Kahlbaum has been calcined and is quite inert to acids. It took up no alizarinic acid from alcoholic solution and did not react with Orange II in aqueous solution. Sulphuric acid (1-20 N) had no action on it in one week. An alumina catalyst was prepared by heating aluminum nitrate in the usual way. It was only colored a faint pink after standing for a week in contact with a saturated solution of alizarinic acid in alcohol.

Alumina was then precipitated from aluminum chloride with a slight excess of ammonia. The precipitate was washed five times by decantation, filtered, and dried partially between filter paper. It was then suspended in sufficient alcohol to form a thick suspension, which was filtered through cheese-cloth to give uniformity. This suspension was evaporated to dryness and the solid heated in an oven at 110° for forty-eight hours. The fine powder required very little grinding before use. The alcohol treatment is useful in dehydrating the gel partly. It thereby prevents the caking which is generally noticed when water suspensions of alumina are dried. A more adsorbent form of alumina was also prepared by precipitating the gel as described and using the alcoholic suspension without further treatment.

Pure sublimed alizarinic acid was dissolved in absolute alcohol. A saturated solution was found on drying to contain about 1.7 mg / cc. The solutions were allowed to stand in stoppered flasks for three weeks at room temperature in contact with 0.2—0.3 g Al_2O_3 . About half the supernatant liquid was removed, centrifuged, and analyzed by the oxidation method described by Weiser.³ The data are given in Table I and Fig. 1, where No. 1 is with dried alumina, Nos. 2 and 3 with two different samples of suspended alumina. In all three cases the concentrations in the solutions vary continuously and we are therefore dealing with adsorption over the ranges covered by the table.

* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

¹ Coll. Symp. Mon., 7, 161 (1930).

² Bull., (3) 25, 862 (1901).

³ J. Phys. Chem., 31, 1824 (1927).

TABLE I
Alumina and Alizarinic Acid in Alcohol
Length of run: three weeks

A = Milligrams alizarinic acid per gram alumina

B = Milligrams alizarinic acid per cc solution

Dried Alumina				Alumina Suspension			
A ₁	B ₁	A ₁	B ₁	A ₂	B ₂	A ₂	B ₂
36.5	0.10	76.5	0.85	116	0.00	116	0.08
34	0.18	95	1.07	200	0.07	139	0.36
45	0.25	81	1.18	202	0.33	132	0.72
53	0.31	125	1.43	248	0.50	163	0.77
72	0.52	102.5	1.47	268	0.72	148	1.02

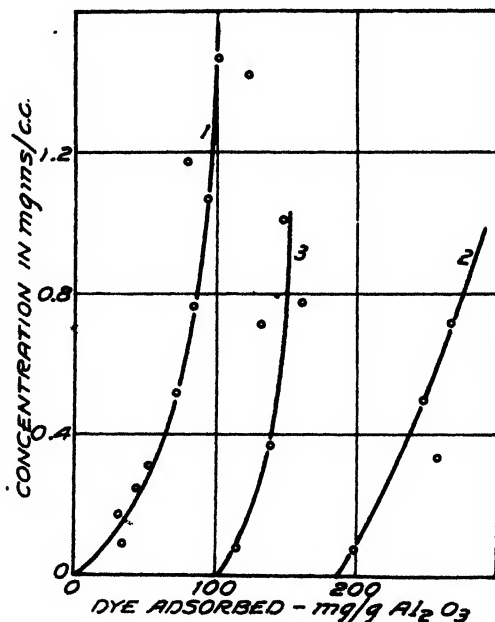


FIG. 1
Alizarinic Acid in Alcohol and Alumina

In Run 2 there is practically complete exhaustion of the bath at low concentrations and it might be claimed that this represented an insoluble compound which then adsorbed alizarinic acid. The simplest answer to this is that 116 mg alizarinic acid per gram alumina corresponds approximately to a formula $\text{Al}_{128}(\text{C}_{14}\text{H}_7\text{O}_4)$, which is absurd.

Since Orange II acid is moderately soluble in water, the first run was made with an aqueous solution and a suspension of alumina prepared by precipitating an aluminum chloride solution with ammonia and washing five times by decantation. The concentrations of the stock solutions and the solutions in

final equilibrium were determined by the titanous chloride titration method of Knecht,¹ which was found to be quite satisfactory. The data are given in Table II.

TABLE II
Alumina and Orange II Acid in Water
Length of run: three weeks

A = Milligrams Orange II acid per gram alumina
B = Milligrams Orange II acid per cc solution

A	B	A	B
66	0.640	2150	0.625
710	0.640	2890	0.625
1163	0.615	3340	0.615
1808	0.640	3980	0.655

The entire range gives a practically constant value for the concentrations of the solutions, thus showing the existence of two phases and confirming the conclusion of Gordon that a definite chemical compound is formed under these conditions. Qualitative observation of the systems during the progress of the reaction bears out this conclusion. The Orange II lake settles out immediately on mixing and is probably then an adsorption complex. After standing for five days at room temperature needle-like crystals could be observed in all the flasks. Some of these crystals were over an inch long. Careful inspection showed that the powdery mass of alumina had been replaced by a mat of crystals. Analyses of some recrystallized samples gave 96.7 percent dye acid instead of 97.3 percent required by AlX_3 . That is close enough for our purposes.

One sample of an aqueous alumina suspension, which was about one year old, was treated with an equal volume of the dye acid. Crystals of the aluminum salt were noticed in a few hours. A sample of alumina prepared by heating aluminum nitrate was treated in the same way. This alumina had been shown previously to have practically no adsorbing power for alizarinic acid. With Orange II acid a slight swelling of the particles was noticeable after forty-eight hours. After standing for two weeks the appearance of the sample was very interesting. The large particles of alumina retained their original form; but small radiating crops of needles seemed to sprout from them. At the end of two months the alumina had disappeared partly and a good deal of crystalline material had formed.

When alumina was treated with aqueous solutions of the sodium salt of Orange II, the result was apparently an adsorption isotherm as shown in Table III and Fig. 2.

¹ Knecht and Hibbert: "New Reduction Methods in Volumetric Analysis" (1925).

TABLE III

Alumina and Sodium Orange II in Water

Length of run: three weeks

A = Milligrams Orange II adsorbed per gram alumina

B = Milligrams Orange II per cc solution

A	B	A	B
411	1.70	1155	5.25
865	3.32	1490	7.02

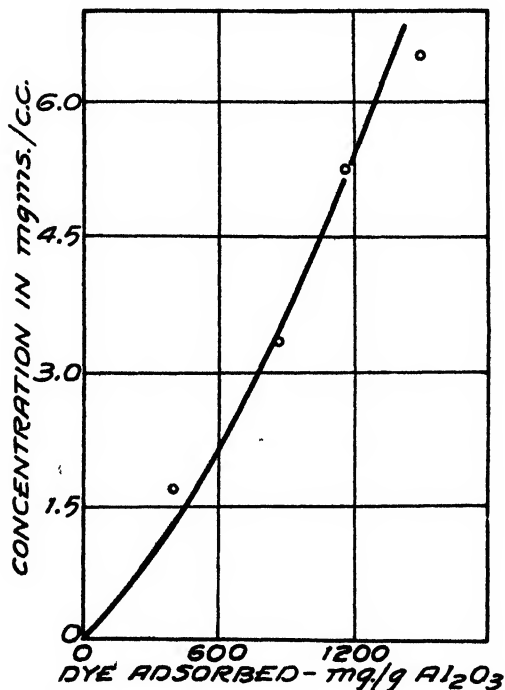


FIG. 2

Sodium Salt of Orange II in Water and Alumina

This unexpected result might be due to one of two causes:

1. Orange II is adsorbed in the form of the sodium salt (the obvious explanation).
2. The dye reacts with alumina to form a definite compound; but the resulting change in caustic soda content is sufficient to cause a variation in the solubility of the compound, which simulates adsorption. The second alternative is ruled out because the pH of the solutions varied between 7.2 and 7.6, whereas, it should have been between 11.0 and 11.8 if all the sodium hydroxide corresponding to the dye had remained in the solution.

On the other hand special analyses showed no decrease in the amount of sodium in the solution. This is analogous to what was found by Weiser for sodium alizarate; the explanation is undoubtedly the same in the two cases.

Our alumina was impure and contained ammonium chloride. The Orange II anions are exchanged for chloride ions and the sodium ions left in solution. If we were to start with a pure alumina, made from amalgamated aluminum, we should undoubtedly get adsorption of the salt of Orange II acid just as was done in the case of sodium alizarate. Unfortunately, time did not permit of this experiment being done at present.

In order to tie in the results with Orange II acid and those with alizarinic acid, a set of experiments was made with alcoholic Orange II acid and an alcoholic suspension of alumina. The results are given in Table IV and Fig. 3.

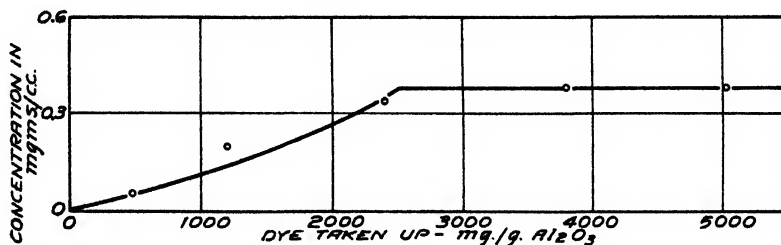


FIG. 3
Orange II Acid in Alcohol and Alumina

TABLE IV
Alumina and Orange II Acid in Alcohol
Length of run: three weeks
A = Milligrams Orange II per gram alumina
B = Milligrams Orange II per cc solution

A	B	A	B
498	0.046	3810	372
1195	0.197	5030	378
2425	0.334		

The curve shows a first portion which seems to indicate adsorption, followed by a flat due to the formation of the chemical compound obtained by Gordon and confirmed by us. It was noticed that crystals of the aluminum salt were plainly visible in the last two reactions flask, while no crystals could be detected in the first three. The alumina, however, was colored orange. Since the aluminum salt of Orange II acid is appreciably soluble in alcohol, the first portion of the curve is of an adsorption curve modified by solubility. For extreme accuracy a correction would have to be made for the amount of aluminum salt in solution. This correction has not been made.

It is not clear why Orange II acid should form a compound readily with alumina while alizarinic acid does not. Orange II is a stronger acid than alizarinic acid; but that is not the whole thing because sulphuric acid, which is a still stronger acid, is adsorbed by alumina from low concentrations in aqueous alcohol.

We hoped to be able to show that alumina precipitated from a sulphate solution would take up less alizarin than alumina precipitated from a chloride solution, because of the greater adsorption of sulphate over chloride. It is well known that some acid dyes which are not affected by sodium chloride can be stripped from wool to some extent by sodium sulphate. This result was not attained because, under the conditions of our experiments, alizarin ions are adsorbed so much more strongly than either sulphate or chloride ions that any difference between the last two is negligible. By adopting a new method of precipitating lakes we were able to get some new and interesting information in regard to alumina-alizarin lakes.

The standard method of making alumina-alizarin lakes is: to precipitate the alumina with ammonia, sodium carbonate, or caustic soda; to wash it several times by decantation or by centrifuging; and then to add the dye to the alumina suspension, usually following this with addition of a solution of calcium acetate to effect more complete precipitation of the dye. Since we wished to study the effect of various salt ions, we substituted for this procedure one which we call the one-step process. This consists in treating a known solution of an aluminum salt with the calculated amount of standard alkali, adding the desired amount of dye immediately. A later improvement by Dr. H. L. Davis is to mix the dye and the alkali, adding this mixture to the solution of the aluminum salt.

The advantages of the one-step method for our purpose are three-fold:

1. It saves the time and loss due to washing.
2. It makes possible the study of the effect of the salts present (NaCl , Na_2SO_4 , etc.).
3. It eliminates practically completely effects due to the ageing of the undyed alumina.

It became apparent at once that, in order to use this method to advantage, we needed to know more about the efficiency of alkali and of dye salts in precipitating alumina from solution in the form of a lake. This problem has been discussed in part in the paper,¹ on "Titration Curves for Aluminum Salts with Alkalies." The results which are now given have to do with the effect of sodium alizarate as a precipitating and dispersing agent.²

The solutions used were normal aluminum chloride and aluminum sulphate, standard 0.25 N sodium hydroxide and 0.024 N (0.012 M) sodium alizarate. Table V shows a preliminary run with constant equivalent amounts of aluminum chloride and aluminum sulphate, and varying amounts of dye and alkali. The solutions were mixed in the order previously described, the total volume was made up to 20 cc, and observations were made at the end of twenty-four hours. The data are given in Table V.

¹ Davis and Farnham: J. Phys. Chem., **36**, 1057 (1932).

² This property of alizarin has been known for some time. Knecht ("Manual of Dyeing," **2**, 574) states that "an excess of alizarin prevents the precipitation of aluminum hydroxide from its salts with ammonia."

TABLE V

Precipitation of Aluminum Salts by Sodium Alizarate and Sodium Hydroxide
One aluminum atom is equivalent to three mols NaOH

A 2 cc N AlCl_3		
Equiv. NaOH	cc dye	Observations
2	2	no precipitate formed
3	2	complete precipitation and exhaustion
4	2	partial precipitation; supernatant liquid light orange
2	4	slight precipitation; no exhaustion
3	4	nearly complete precipitation; supernatant liquid slightly yellow
4	4	partial precipitation; exhaustion not complete; supernatant liquid light red
B 2 cc N $\text{Al}_2(\text{SO}_4)_3$		
2	2	nearly complete precipitation; supernatant liquid light orange
3	2	complete precipitation and exhaustion
4	2	partial precipitation; dark red lake; supernatant liquid light orange
2	4	practically complete precipitation; supernatant liquid light orange
3	4	complete precipitation and exhaustion
4	4	partial precipitation; supernatant liquid light orange

An examination of Table V shows that the precipitation range for the sulphate lakes is wider than that for the chloride lakes, which is in accord with what had been found previously for the action of alkali alone upon aluminum salts. Sodium alizarate behaves in general something like sodium hydroxide, causing precipitation in small amounts and dispersion in large amounts.

In Table VI are given results when the aluminum chloride or sulphate was kept constant at 2 cc, and the caustic soda at two equivalents, while the amount of dye varied. In order to simplify the tabulation, the following symbols are used for describing the tubes:

1. Indicates a clear solution; red with no precipitate.
2. Indicates partial precipitation of alumina.
 - a) complete exhaustion.
 - b) incomplete exhaustion.

(degree of exhaustion is indicated by minus signs for very slight color in the supernatant liquid and by plus signs for much color).

3. Indicates complete precipitation of alumina.
 - a) complete exhaustion.
 - b) incomplete exhaustion.

It is somewhat difficult to judge between 2 and 3. The variation in the volume of the precipitate was used as a preliminary indication and confirmed by testing the liquid with ammonia.

TABLE VI

Precipitation and Peptization of Alumina Lakes by Varying Concentrations of Sodium Alizarate

A = 2 cc N AlCl_3 ; B = 2 cc N $\text{Al}_2(\text{SO}_4)_3$

Equivalents of sodium hydroxide = 2

O = observations after twenty-four hours

cc dye	O-A	O-B	cc dye	O-A	O-B
1	2b	2a	7	1	1
2	3a	3a	8	1	1
3	2b	2b +	9	1	1
4	1	1	10	1	1
5	1	1	11	1	1
6	1	1	12	1	1

At the end of twenty-four hours all those tubes which did not give clear, colorless, supernatant solutions (those not marked 2a or 3a) were treated as follows:

Five cc of the supernatant liquid were drawn off and placed in a small test-tube. To the aluminum chloride solutions there were added 5 cc of saturated sodium chloride solution, while an equivalent amount of saturated sodium sulphate solution was added to the aluminum sulphate solutions. The tubes were stoppered, shaken, and examined after having stood for twenty-four hours. This use of two different salt solutions is not the usual procedure. In these experiments the object was to have the two systems exactly comparable except for one variable, the inorganic anion. By using the same anion in the aluminum salt and in the added salt it is possible to observe the difference due to only one cause with no complicating factors to consider, such as would result if we used chloride and sulphate initially and sulphate finally in both cases. This would give in one case three competing anions, sulphate, hydroxyl, and alizarate; in the other case four, sulphate, hydroxyl, alizarate, and chloride. The results are given in Table VII.

TABLE VII

Flocculation of Peptized Alumina-Alizarin Lakes

A = aluminum chloride lakes with sodium chloride

B = aluminum sulphate lakes with sodium sulphate

O = observations after twenty-four hours

cc dye = concentration of dye per 20 cc in original

cc dye	O-A	O-B	cc dye	O-A	O-B
1	3a	—	7	*	1
2	—	—	8	*	1
3	3a	3a	9	*	1
4	3a	3a	10	3b	3b
5	3a	3b---	11	3b	2b ⁺
6	3b---	3b---	12	2b(?)	2b ⁺⁺

* These tubes show the full red color; but a partial precipitation of the lake can be detected by a cloudiness at the bottom of the tubes.

All tubes containing more than 3 cc dye fail to form precipitated lakes. This is due to the fact that the dye anions, being adsorbed strongly, exert a peptizing action upon the lake which is comparable with that of excess sodium hydroxide. For alumina alone about 4.2 equivalents of alkali are sufficient to redisperse alumina in an aluminum chloride system, while 4.7 equivalents is needed for the sulphate system. If we consider 4 cc of dyes being the first completely redispersed system in the presence of two equivalents of caustic soda, we must then assume that 4 cc of the dye are equivalent to at least 2.2 NaOH. Since the dye solution is 0.024 normal, 4 cc = 0.0096 normal cc. 2 equivalents of NaOH = 1.33 normal cc per 2 cc AlCl_3 . 4.2 equivalents of NaOH = 1.4 cc and $1.33 + 0.096 = 1.429$ cc. It is thus evident that the dye solution is about equivalent in peptizing power to the same amount of sodium hydroxide. This knowledge is very useful in the preparation of alizarin lakes by the one-step process.

In the chloride suspensions of alumina a positively charged lake is formed in the presence of 1 cc of dye. This is due to the fact that an excess of aluminum chloride is present, the peptizing power of the strongly adsorbed, trivalent aluminum ion overcoming the effect of the weakly adsorbed chlorine ions and stabilizing the sol. In the sulphate solutions the bivalent sulphate ions are adsorbed strongly enough on the acid side to prevent this action.

The addition of sodium chloride or sodium sulphate flocculates the sols resulting from the presence of an excess of dye, even though these are negatively charged sols. The flocculation must be due to an adsorption of sodium ions in preference to chlorine and sulphate ions. With the negatively charged sols there is thus a reversal of the anion effect, sodium sulphate having less flocculating power than sodium chloride because sulphate ion is adsorbed more strongly than chloride ion and therefore tends to keep the sol more negative. This is identical with what was observed years ago with albumin sols. Both alumina sols show a region of maximum stability on addition of a definite amount of sodium chloride or sulphate. For this concentration this region occurs with 7-9 cc dye. The sulphate sols remain perfectly clear for twenty-four hours after the addition of salt, while the chlorides are precipitated partially. Beyond this range is another of comparatively low stability, followed by a third, stable, re-peptization zone. This is a striking example of the well-known irregular series.¹

It is easy to see that the action of alkali on aluminum sulphate and aluminum chloride should produce a precipitate at lower concentrations in the sulphate solutions; but it is not at all clear why more alkali is necessary to peptize the alumina from the sulphate solution. It should be the other way round. This probable explanation is that the difference is apparent and not real, being due to the fact that the alumina from the sulphate solution is much denser and is apparently less hydrous than that from the chloride solution.

Bancroft and Ackerman² have accounted for the polygenetic nature of alizarin with different mordants by postulating the presence of yellow, un-

¹ Kruyt and van Klooster: "Colloids" (1927).

² J. Phys. Chem., 35, 2568 (1931).

dissociated alizarinic acid, red alizarate ion, and purple undissociated sodium alizarate. Dr. H. L. Davis has pointed out to us that it would be more in line with the views of Hantzsch¹ to postulate the existence of several, colored, tautomeric, alizarinic acids. Sørensen² describes the use of alizarin as an indicator. He records two distinct color changes: yellow to red at pH 5-5.6.8, and violet to purple at pH 10.1-12.1; the change from red to violet is gradual. By very careful addition of alkali to a dilute solution of alizarinic acid, one easily obtains all four colors: yellow, red, violet and purple (blue). Even assuming that the violet form is a mixture of red and the blue, there are three, distinct, colored forms of alizarinic acid, and it is necessary to assume some tautomeric changes to account for these differences.

The nature of the solvent often has a great effect on the equilibrium between two forms, but it should have no effect on the nature of the form crystallizing from the solution, provided the crystals do not contain solvent of crystallization. Meyer and Jacobson,³ not knowing the phase rule, state that alizarinic acid crystallizes in yellow crystals from alcohol, but in orange-red crystals from other organic solvents. Special experiments showed that solutions of alizarinic acid in chloroform, carbon tetrachloride, ether, *n*-butyl bromide, and paraldehyde are yellow, solutions in alcohol and acetone are orange-yellow, and solutions in benzaldehyde are orange. Alizarin crystallized from these solvents in yellow to yellow-orange crystals, depending on the size of the crystals. When powdered, all the crystals were the same yellow.

The behavior of a pyridine solution is interesting. In pure, dry pyridine alizarin dissolves to form a yellow solution. On dilution with a small amount of water the solution becomes red, changing to purple as still more water is added. This change is in the direction one would expect from increasing alkalinity.

If the polygenetic character of alizarin is due to tautomerism and if this tautomerism is affected by the pH of the solution, it should be possible to change the color of alizarin lakes by varying the pH. Experiments were therefore made with alumina and tin lakes.

It was found possible by special manipulations to change the color of the alumina-alizarin lake through the entire series from yellow to violet and back to red. The alumina was prepared by heating aluminum nitrate. While this alumina does not take up much alizarin, it has the advantage of not being peptized readily by acid or alkali. A dilute solution of alizarinic acid in alcohol was treated with a slight excess of caustic soda. While sodium alizarate is not very soluble in alcohol, a purple, apparently clear, solution can be obtained. When shaken with alumina a lavender lake was obtained, which changed to pink on washing with water. Washing with a three percent tartaric acid solution changed the color to yellow. Washing with caustic soda solution restored the original lavender color. A red lake was prepared by treating alumina with alcoholic alizarinic acid. When treated with a solution of phosphoric acid, the lake became yellow. Washing with caustic soda solution changed the lake to a violet red.

¹ Cf. Heinrich (Johnson and Hahn): "Theories of Organic Chemistry," 382-478 (1922).

² Biochem. J., 21, 241 (1909).

³ "Lehrbuch der organischen Chemie," 2, II, 555 (1903).

Tin mordant was prepared by the method described by Ackerman. It was suspended in alcohol and treated with an alcoholic solution of alizarinic acid. A yellow lake was formed. The mixture was made alkaline with ammonia, after which acetic acid was added drop by drop until a red shade resulted. On filtering, a red lake was formed which was fairly deep in color and reasonably fast to washing with alcohol and water. The color is actually more nearly an orange red than the cherry red of the alumina lakes. With sodium alizarate and alkali tin gives a purple lake.

We see that alumina lakes are red over a wide range of pH; but can be obtained yellow or purple. With stannic oxide the red lake exists only over a narrow range of pH, the yellow occurring over most of the acid range and the purple over most of the alkali range. With other mordants one would probably get ranges intermediate between these two extremes.

The general results of this investigation are:

1. By using alcohol as a solvent it is possible to make a phase rule study of alizarinic acid and alumina.
2. Kahlbaum's alumina is practically inert towards alizarin. Alumina obtained by heating aluminum nitrate adsorbs alizarin slightly. A precipitated alumina dried at 100° is a moderately good adsorbent. Freshly precipitated, washed alumina is a good adsorbent.
3. At ordinary temperatures alizarin forms no definite chemical compound with alumina. The alumina-alizarin lakes are adsorption complexes. This confirms the results of Weiser and Porter.
4. Orange II acid forms a definite chemical compound, AlX_3 , with alumina both in aqueous and in alcoholic solution. This confirms the results of Reinmuth and Gordon. At low concentrations Orange II acid is adsorbed by alumina. This was not discovered by Reinmuth and Gordon, who did not study this range.
5. The sodium salt of Orange II is adsorbed by alumina, no definite chemical compound being formed. This was not discovered by Reinmuth and Gordon.
6. Caustic soda and sodium alizarate have been shown to be nearly equivalent in the precipitation and dispersion of alumina.
7. The negatively charged lakes formed by peptization with sodium alizarate are destabilized by sodium chloride and sodium sulphate owing to adsorption of sodium ions. There is a reversal of the order of the anions just as there is with albumin.
8. The color of an alizarin solution can be varied over the entire range from yellow to red to violet (to blue) by a progressive increase in pH. Since this is apparently due to tautomeric changes, one must at least assume the existence of yellow, red, and blue (purple) alizarinic acids.
9. The colors of alizarinic acid dissolved in pyridine can be varied through the entire range by adding water which increases the alkalinity.
10. Under suitable conditions one can prepare alumina and tin lakes of all the colors. With alumina the red is stable over a wide range of pH and with tin over a narrow range.

ELECTROKINETICS XII. INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS II. Al₂O₃—ORGANIC LIQUID INTERFACES*

BY OTTO G. JENSEN AND ROSS AIKEN GORTNER

Introduction

Considering the ultimate electrical nature of matter, it is logical to expect that measurements of the electrical properties of a molecule would prove fruitful in elucidating its structure. This has proved to be the case. Determinations of the dielectric constants of organic compounds have been numerous. In themselves, they are of limited value, but together with density and refractive index determinations, they play an important part in the newer theories of the structure of matter. The dipole moment of a molecule is a measure of its electrical asymmetry. Phenomena such as molecular association and adsorption are caused by the stray electric fields of molecules resulting from a lack of balance amongst their electrical components.

This study is concerned with the measuring of these unbalanced electrical forces at the boundary of two contiguous phases. More specifically, it is a study of the molecular structure of certain organic compounds by means of streaming potential technic.

Historical

The literature has been already adequately reviewed by Briggs,¹ Bull and Gortner,² and Martin and Gortner³ in earlier papers in this series, so that only the more recent contributions need mention.

Most of the records in the literature are expressed in terms of the electrokinetic potential (ζ -potential) calculated by the formula

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon} \quad (1)$$

where η = coefficient of viscosity, H = observed E.M.F., κ_s = specific conductance of the liquid in the diaphragm, P = hydrostatic pressure, ϵ = dielectric constant.

Bull and Gortner^{2,4} have determined the effect of different electrolytes in various concentrations on the ζ -potential, the density of charge, and the

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¹ J. Phys. Chem., **32**, 641-675 (1928).

² J. Phys. Chem., **35**, 309-330 (1931).

³ J. Phys. Chem., **34**, 1509-1539 (1930).

⁴ J. Phys. Chem., **35**, 700-721 (1931).

thickness of the double layer. They found that, in general, the ζ -potential decreased with increasing concentration, but that the charge per unit area of surface increased. They point out that, at least for univalent ions, the discharging of colloidal particles may be due more to a decrease in the thickness of the double layer than to an actual diminishing of the charge. They were unable to detect any antagonistic action between NaCl and KCl, NaCl and CaCl_2 , or CaCl_2 and MgCl_2 . They point out that the calculated ζ involves a knowledge of the dielectric constant, which in the adsorbed film is probably different from the bulk value. They accordingly propose⁵ that, instead of ζ , electrokinetic measurements be expressed in terms of qd , the *electric moment per unit area*, which can be calculated using only the experimentally determined values by the formula

$$qd = \frac{\eta \kappa_s H}{P} \quad (2)$$

where q is the charge per unit area of the double layer and d is its thickness, the other quantities being the same as in equation (1), all expressed in electrostatic units.

Determinations of the electrokinetic potentials at solid-organic liquid interfaces have not been numerous. Quincke⁷ was the first one to study the electro-endosmose of organic liquids. He found that turpentine was negatively charged in respect to asbestos, clay, quartz, shellac, and silk, whereas water was positively charged. The work of Strickler and Mathews⁸ shows that Coehn's⁹ rule does not hold for the organic solvents which they studied, but that the dielectric constant ratio does affect the magnitude of flow. They made no attempt to correlate their findings with the structure of the compounds.

Martin and Gortner³ have obtained striking correlations between the electrokinetic potentials at cellulose-organic liquid interfaces, as obtained by streaming potential measurements, and the molecular structure of the organic compounds. For a homologous series of normal aliphatic alcohols, the introduction of a $-\text{CH}_2$ group into the chain changes the ζ -potential approximately ± 36 millivolts. The substitution of a methyl group for a hydrogen atom to form a branched-chain alcohol alters the ζ -potential to the extent of only ± 4 millivolts. Benzene gave no streaming potential. In the case of substitution for a hydrogen atom in the benzene molecule, the groups affected the ζ -potential in the following order: $\text{CH}_3 < \text{Cl} < \text{Br} < \text{NH}_2 < \text{NO}_2$.

Fairbrother and Balkin¹⁰ have made a careful study of the electro-endosmose of 14 pure organic liquids through a diaphragm of sintered Jena Geräte glass powder. They conclude that there is a very close relationship between the electro-endosmotic velocity of an organic compound and its dipole moment.

⁵ Bull and Gortner: *Physics*, 2, 21-32 (1932).

⁷ Pogg. Ann., 113, 513-598 (1861).

⁸ J. Am. Chem. Soc., 44, 1647-1662 (1922).

⁹ Wied. Ann., 64, 217-232 (1898).

¹⁰ J. Chem. Soc., 389-403 (1931).

Experimental

The problem.—In the light of the findings of Martin and Gortner,² it was thought that a further investigation into the relationship between molecular configuration and interfacial energy might prove fruitful. The present report deals with such a study using (1) an homologous series of 5 normal aliphatic acids, (2) an homologous series of the normal aliphatic alcohol-esters of acetic acid and (3) a series of the ethyl esters of certain of the normal aliphatic acids, against aluminum oxide.

The chemicals used may be expressed as (1) $R\text{---COOH}$, (2) $\text{CH}_3\text{---CO---O---R}$ and (3) $R\text{---CO---O---C}_2\text{H}_5$ where R stands for a series of straight chain aliphatic radicals differing from each other by $\text{---CH}_2\text{---}$. If the electrokinetic effect at the interface is produced by the unbalanced polarity of the molecules oriented at the interface, as suggested by Martin and Gortner,² then it should be interesting to observe the relative effect on such a measurement when a given radical is attached (1) directly to the carbon of a carbonyl group or (2) when it is separated from the carbonyl group by the oxygen of an ester linkage.

The method.—Streaming potential apparatus essentially identical with that used by Martin and Gortner² was used. Since this has been adequately described by them, the description will not be repeated. Two modifications of the apparatus were found necessary.

Because of the high voltages which were produced by the streaming liquid, it became necessary to insert four 6-volt lead-acid storage batteries (automobile type) and three units of 48-volt lead-acid storage batteries (radio B-battery type), connected in series, to be used as a potential source to be balanced through the potentiometer against the E.M.F. generated by the streaming liquid, using the quadrant electrometer as a null instrument. It was thus possible to accurately measure streaming potential E.M.F.'s as great as 150 volts.

The second modification dealt with the method for measuring the specific conductivity of the liquids in the pores of the diaphragm. It was discovered that the resistances of most of the liquids in the diaphragm were too large to be measured with the ordinary Wheatstone bridge using either a 1000-cycle current and telephones or a 60-cycle current and an alternating current galvanometer of 0.025 microampere sensitivity. Accordingly, the apparatus was so designed that the resistance measurements could be made by a direct current method, employing the electrometer as the null-point instrument. Potentials of approximately 150 volts were applied to the bridge arm containing the cell to balance the current furnished by the potentiometer and passing through a standard megohm resistance.

The arrangement of apparatus for measuring the resistance of the diaphragm containing the organic liquid is given in Fig. 1. Zero deflection of the electrometer E is obtained by balancing the current through the diaphragm D under the potential of B , against the current through the standard megohm resistance R under the potential at A . B is a 150-volt storage battery, and

the potential at *A* is led off from a L. and N. type K potentiometer. The ratio of the potentials required, B/A , is equal to the resistance of *D* in megohms, the resistance of *A* and *B* being neglected. Reversing the polarities, repeating the determination, and averaging the results, obviates any error arising from a potential produced in the cell caused by a difference in the levels of the liquid.

For the determination of the cell constant, the liquid is removed and the diaphragm washed three times with ethyl alcohol and three times with portions of the 0.1 *N* KCl solution to be used for the determination. The cell is now introduced into one arm of a Wheatstone bridge and the determination completed in the usual manner, using a 60-cycle current and an alternating current galvanometer as a null-point instrument.

Aluminum oxide* which had been exhaustively extracted through a period of several months with many liters of distilled water, during the whole of which time it was in contact with a large volume of water, was used as the diaphragm material. Prior to use, it had been dried at 110° for 72 hours.

Twenty-four hours before the determination was to be made, sufficient aluminum oxide to fill the glass cell was suspended in the liquid to be studied. The aluminum oxide was then packed into the cell by tamping with a glass rod.

Two perforated gold electrodes were placed at each end of the diaphragm, and between the double electrodes there was inserted a disk of fine cloth (batiste) to prevent the aluminum oxide sifting through the perforations. No error was introduced by this procedure, for the leads from the two electrodes on the same side of the diaphragm were "shorted" by being placed into the same mercury cup. Cork gaskets were employed between the electrodes and between the electrodes and the glass parts. The cell was then filled with the liquid to be studied, placed in the constant temperature bath, and connected to the pressure line.

After a lapse of one-half hour to allow the cell to assume the temperature of the bath, streaming potentials were determined. All of the determinations were made at 30°C.

Calculation of Results.

(A) *Constants Employed.* In Table I are given the values for ϵ the dielectric constant, η the coefficient of viscosity, and μ the dipole-moment used in calculating the values presented in Tables II to XVII.

The values for ϵ and η have been taken from the Critical Tables with the exception of those values for η which bear an asterisk. These were determined by means of an Ostwald type viscometer. The values for μ are those compiled by Smyth.¹¹

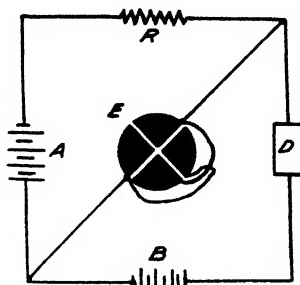


FIG. 1

Diagrammatic arrangement of the bridge for the measurements of high resistivity.

* Our thanks are due Dr. Francis Frary of the Aluminum Company of America for providing us with a large sample of aluminum oxide.

¹¹ "Dielectric constant and molecular structure" (1931).

TABLE I

Liquid	ϵ	η	$\mu(\times 10^{18})$
Acetic acid	6.2	0.0104	1.4
Methyl acetate	6.7	0.00344	1.75
Ethyl acetate	6.25	0.00401	1.80
n-Propyl acetate	6.2	0.00513	1.86
n-Butyl acetate	5.0	0.00658*	1.85
n-Amyl acetate	4.95	0.00757*	1.91
Ethyl formate	7.0	0.00375	1.93
Ethyl n-propionate	5.7	0.00473	1.79
Ethyl n-butyrate	5.1	0.00604	—
n-Propionic acid	3.2	0.00963	1.74
n-Butyric acid	2.8	0.0134	0.9
n-Valeric acid	2.6	0.0186	—
n-Caproic acid	3.2	0.0256	—

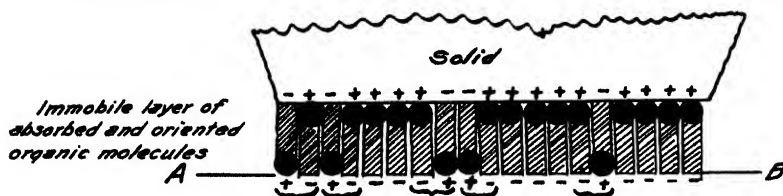


FIG. 2

A diagrammatic representation of the oriented adsorption of organic dipoles at a solid liquid interface. Postulated as a source of the electric double layer.

(B) *Calculation of Electrokinetic Potential (ζ)*. The zeta potential is calculated from the formula, $\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon}$. To express ζ in millivolts, $\zeta = 847,649 \frac{\eta H\kappa_s}{P\epsilon} \times 10^6$, where η = coefficient of viscosity, H = streaming potential in volts, κ_s = specific conductivity of the liquid in the diaphragm in reciprocal ohms, P = pressure in centimeters of mercury, ϵ = dielectric constant of the liquid.

(C) *Calculation of Electric Moment of the Double Layer (qd)*. The electric moment for a unit area of the double layer is calculated from the formula, $qd = \eta H\kappa_s / P$. To express qd in electrostatic units, $qd = 226,200 \eta H\kappa_s / P$, where η , H , κ_s and P have the same meaning as above.

(D) *Unbalanced Orientation of the Molecules in the Interface*. Martin and Gortner³ have suggested that the electrokinetic potential at a solid-organic liquid interface arises from an oriented adsorption of organic molecules. If organic dipoles are oriented at an interface, we might expect an arrangement more or less like that shown diagrammatically in Fig. 2. Assuming a plane of sheer at A-B, the bracketed pairs of dipoles, oriented in opposite directions, might be expected to neutralize each other, whereas the "unbalanced orientation" of the remaining molecules should give rise to a net negative charge on the "immovable layer" side of the interface with a corresponding positive charge in the streaming liquid.

On this hypothesis, it should be possible to calculate the percentage of "unbalanced orientation" of the organic molecules in the immovable layer assuming (1) a monomolecular, close-packed, oriented layer, and (2) that the electric moment per unit area of the double layer is the product of the dipole moment of the organic molecule and the number of "unbalanced" molecules oriented per unit area.

In our calculations, the values for the cross-sectional area of the molecules (A) are those given by Rideal¹² for the limiting areas per molecule in the liquid condensed form. For esters $A = 22.0 \text{ \AA}^2$ and for acids $A = 24.4 \text{ \AA}^2$.

The per cent of the total surface occupied by oriented but "unbalanced" molecules is given by the expression, $qd A / \mu 10^{14}$, where μ is the dipole moment, and qd and A have the meaning denoted above.

Presentation of Data

The streaming potentials at various pressures for the fifteen liquids studied are presented in Tables II to XVI. In the formula, $\zeta = 4\pi\eta H\kappa_a / P\epsilon$, it is assumed that H/P is a constant. The validity of this assumption is demonstrated by the values in the third column of each table. Included is the specific conductivity of the liquid in the diaphragm (κ_a) and the calculated values for the zeta potential, the electric moment of the double layer, and the percent of the "unbalanced" oriented molecules in the interface. The sign of the charge on the aluminum oxide phase is given parenthetically. Table XVII summarizes these values. They are shown graphically in Fig. 3 and 4.

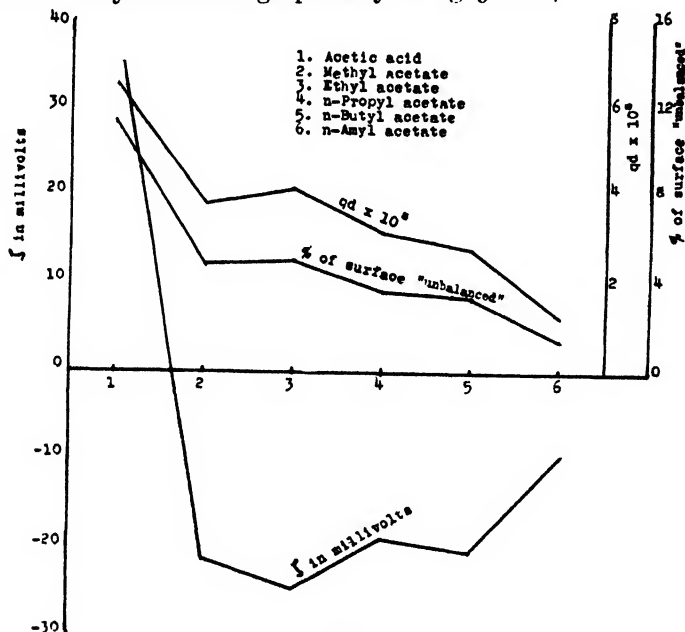


FIG. 3

The electrokinetic potentials, the electric moment per unit area, and the percent of "unbalanced" oriented molecules at an Al_2O_3 —organic liquid interface for a series of the n-aliphatic esters of acetic acid.

¹² "Surface Chemistry," 100 (1930).

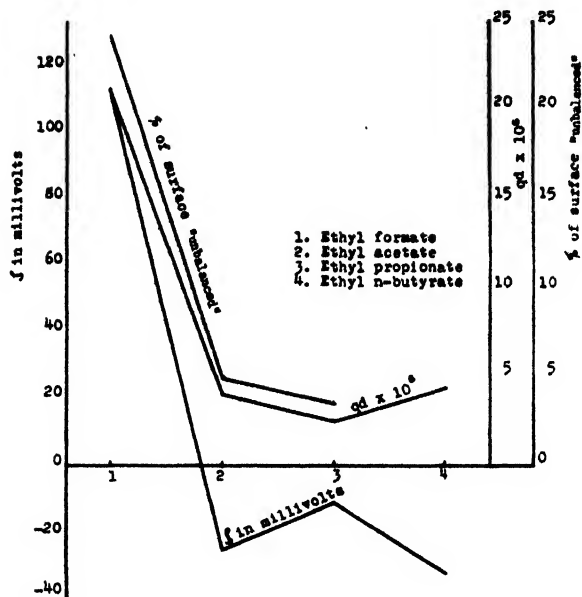


FIG. 4

Data similar to that shown in Fig. 3 for an Al_2O_3 —organic liquid interface for a series of the ethyl-esters of certain of the n-aliphatic acids.

TABLE II

Data for Acetic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v) \bar{P} (cm Hg)
65.4	0.6826	0.104	101.0	1.2511	0.124
77.0	0.8839	0.115	111.0	1.2881	0.116
84.3	0.9720	0.115	160.5	1.9790	0.123
92.5	1.0812	0.117	Average = 0.116		

$\kappa_s = 2.39 \times 10^{-7}$, $\zeta = 39.4$ m.v., $qd = 6.52 \times 10^{-5}$, "Unbalanced" oriented molecules = 11.4%.

TABLE III

Data for Methyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v) \bar{P} (cm Hg)
255.0	66.020	2.59	68.8	18.670	2.71
227.3	57.625	2.54	52.5	14.000	2.67
173.7	45.655	2.63	35.1	9.668	2.75
131.7	35.090	2.66	19.8	5.596	2.83
99.5	26.870	2.70	Average = 2.68		

$\kappa_s = 1.86 \times 10^{-8}$, $\zeta = 21.7$ m.v., $qd = 3.88 \times 10^{-5}$, "unbalanced" oriented molecules = 4.88%.

TABLE IV

Data for Ethyl Acetate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)
13.3	21.235	15.97	49.8	79.69	16.00
18.0	29.00	16.11	63.8	102.70	16.10
27.0	43.42	16.08	73.6	118.30	16.07
38.8	62.21	16.03	Average = 16.06		

$\kappa_s = 2.84 \times 10^{-9}$, $\zeta = 24.8$ m.v., $qd = 4.14 \times 10^{-5}$, “unbalanced” oriented molecules = 5.05%.

TABLE V

Data for n-Propyl Acetate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)
15.6	22.605	14.49	50.5	72.590	14.37
21.0	30.235	14.40	60.2	90.140	14.97
25.6	36.750	14.36	66.1	97.970	14.82
32.3	45.940	14.22	71.8	108.920	15.17
40.6	59.750	14.71	76.7	114.300	14.90
Average = 14.64					

$\kappa_s = 1.87 \times 10^{-9}$, $\zeta = 19.2$ m.v., $qd = 3.17 \times 10^{-5}$, “unbalanced” oriented molecules = 3.75%.

TABLE VI

Data for n-Butyl Acetate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)
18.4	53.14	28.88	29.7	90.00	30.30
19.5	57.64	29.57	31.5	93.96	29.83
20.8	60.70	29.18	34.3	102.29	29.82
23.3	70.00	30.04	38.4	114.95	29.93
24.7	72.57	29.38	Average = 29.66		

$\kappa_s = 6.23 \times 10^{-10}$, $\zeta = 20.6$ m.v., $qd = 2.75 \times 10^{-5}$, “unbalanced” oriented molecules = 3.27%.

TABLE VII

Data for n-Amyl Acetate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F. (v.) $\frac{P}{P}$ (cm Hg)
25.1	8.28	3.30*	108.0	72.50	6.71
62.9	41.65	6.62	121.5	84.70	6.97
50.4	36.41	7.22	141.3	104.03	7.36
83.7	59.37	7.09	Average = 7.00		

* Omitted in calculation of average.

$\kappa_s = 1.05 \times 10^{-9}$, $\zeta = 9.53$ m.v., $qd = 1.26 \times 10^{-5}$, “unbalanced” oriented molecules = 1.45%.

TABLE VIII

Data for Ethyl Formate—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
33.0	.1024	.0310	120.6	.3582	.0297
48.4	.1440	.0292	156.0	.4705	.0302
65.2	.1880	.0288	207.0	.6295	.0304
74.3	.2150	.0289	246.5	.7500	.0304
94.4	.2670	.0283	303.0	.9221	.0304
Average = .0297					

$\kappa_s = 8.41 \times 10^{-6}$, $\zeta = 113$ m.v., $qd = 21.2 \times 10^{-5}$, "unbalanced" oriented molecules = 24.1%.

TABLE IX

Data for Ethyl Propionate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
36.8	46.05	12.51	64.2	80.10	12.47
41.2	51.53	12.51	72.4	90.97	12.56
48.6	61.95	12.75	78.9	98.25	12.45
55.0	68.32	12.42	Average = 12.52		

$\kappa_s = 2.17 \times 10^{-9}$, $\zeta = 10.8$ m.v., $qd = 2.90 \times 10^{-5}$, "unbalanced" oriented molecules = 3.56%.

TABLE X

Data for Ethyl n-Butyrate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
42.2	30.66	7.26	69.0	50.80	7.36
53.5	41.75	7.80	77.4	54.45	7.03
60.4	46.09	7.63	Average = 7.42		

$\kappa_s = 4.30 \times 10^{-9}$, $\zeta = 32.1$ m.v., $qd = 4.36 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value of μ is lacking.

TABLE XI

Data for Propionic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
21.5	30.13	14.01	48.2	61.63	12.79
31.8	44.45	13.98	55.5	71.11	12.81
36.9	46.65	12.64	72.2	80.63	11.17
42.0	54.50	12.98	86.6	95.76	11.06
Average = 12.68					

$\kappa_s = 5.77 \times 10^{-10}$, $\zeta = 18.66$ m.v., $qd = 1.67 \times 10^{-5}$, "unbalanced" oriented molecules = 2.34%.

TABLE XII

Data for n-Butyric Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
30.0	34.93	11.64	66.6	67.82	10.18
39.3	42.56	10.83	75.8	77.38	10.21
48.6	51.49	10.59	86.3	86.00	9.97
54.7	56.01	10.24	Average = 10.52		

$\kappa_s = 4.07 \times 10^{-9}$, $\zeta = 173.7$ m.v., $* qd = 13.0 \times 10^{-5}$, "unbalanced" oriented molecules = 35.2%.

* See footnote to Table XVII.

TABLE XIII

Data for n-Valeric Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
30.2	13.60	4.50	73.4	38.51	5.25
33.6	14.37	4.28	84.8	44.94	5.21
36.2	14.55	4.02	98.2	54.16	5.52
56.2	27.58	4.85	107.7	61.35	5.69
Average = 4.92					

$\kappa_s = 4.06 \times 10^{-10}$, $\zeta = 12.1$ m.v., $qd = 0.84 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value of μ is lacking.

TABLE XIV

Data for n-Caproic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)	Pressure in mm Hg	E.M.F. in volts	E.M.F.(v.) \bar{P} (cm Hg)
29.9	47.08	15.75	67.7	101.75	15.03
40.0	61.46	15.37	73.7	106.02	14.39
52.7	82.54	15.66	78.7	111.41	14.16
58.2	88.59	15.22	94.0	128.13	13.63
Average = 14.90					

$\kappa_s = 2.87 \times 10^{-10}$, $\zeta = 29.0$ m.v., $qd = 2.48 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value for μ is lacking.

TABLE XV

Data for Benzene—Aluminum Oxide Interface

Pressure in mm Hg	E.M.F. in volts
35.3	0
66.0	0

There is a small erratic potential, + or -, at times, but for the greater part of the time there is no E.M.F. It is concluded that impurities cause the spurious potentials and that the zeta potential for a benzene-aluminum oxide interface is zero.

TABLE XVI

Data for Carbon Tetrachloride—Aluminum Oxide Interface

Pressure in mm Hg	E.M.F. in volts
40.3	0
200.0	0

The electrometer needle drifts slowly in one direction and then in the other, but it is concluded that this is due to stray currents or else to slight impurities in the cell. Accordingly the zeta potential for a carbon tetrachloride-aluminum oxide interface is zero.

TABLE XVII

Summary of Data in Tables II to XVI

Table	Liquid	ζ -potential	qd ($\times 10^8$)	Unbalanced orientation of molecules in interface %
II	Acetic acid	+ 39.4	6.52	11.4
XI	n-Propionic acid	+ 18.66	1.67	2.34
XII	n-Butyric acid	+ 173.7*	13.0	35.2
XIII	n-Valeric acid	+ 12.1	0.84	—
XIV	n-Caproic acid	+ 29.0	2.48	—
III	Methyl acetate	— 21.7	3.88	4.88
IV	Ethyl acetate	— 24.8	4.14	5.05
V	n-Propyl acetate	— 19.2	3.17	3.75
VI	n-Butyl acetate	— 20.6	2.75	3.27
VII	n-Amyl acetate	— 9.53	1.26	1.45
VIII	Ethyl formate	+ 113	21.2	24.1
IV	Ethyl acetate	— 24.8	4.14	5.05
IX	Ethyl n-propionate	— 10.8	2.90	3.56
X	Ethyl n-butyrate	— 32.1	4.36	—
XV	Benzene	0	0	0
XVI	Carbon tetrachloride	0	0	0

* This value may be +17.37. A value of 173.7 is obtained providing the value for κ_s is 4.07×10^{-9} (Table XII). The corresponding values for propionic acid and valeric acid are 5.77×10^{-10} and 4.06×10^{-10} respectively. If an error was made in recording the resistivity data on butyric acid and the exponents were 10^{-10} instead of 10^{-9} the value of ζ would be 17.37 instead of 173.7. This appears probable.

If ζ were 17.37, the value for qd would correspondingly be 1.30 and the "unbalanced" orientation would be 3.52%. The series would thus become essentially regular. Since a slight change in the absolute specific conductivity makes these large changes in the determined constants, it is perhaps permissible to call attention to the data of Fairbrother and Balkin,¹⁰ who, in their electro-endosmotic study of glass-organic liquid interfaces, state that "a value of (κ) = $< 1 \times 10^{-8}$ indicates that the conductivity of the liquid in question was too small to be measured, with the apparatus in use at the time." Propionic acid is one of the liquids which they list as having a specific conductivity of less than 1×10^{-8} . While it is not specifically stated, presumably they used $\kappa = 1 \times 10^{-8}$ in calculating their values of ζ . Unfortunately, their data as presented do not permit a recalculation to determine this point. If we were to use for our data a value of $\kappa_s = 1 \times 10^{-8}$, instead of 5.77×10^{-10} as experimentally determined, we should have found that $\zeta = +322.9$ instead of the value of +18.66 m.v. which we report.

Discussion of Results

The streaming potentials obtained in these studies are greater than those observed by others, but it is to be emphasized that this is not due to any peculiarity in the structure of the compounds investigated. The specific conductivity of the liquid in the diaphragm is approximately the same as that of the liquid in bulk. No effort has been made to make an exact determination of the amount of surface conductance, but the results indicate that it is not large, which is to be expected, for the specific surface of the aluminum oxide is relatively low. Martin and Gortner³ report specific conductivities which are more than a thousand times as great as the conductivities of the liquids in bulk. This can be accounted for only by the fact that the cellulose composing the diaphragm plays a major rôle in the conduction of the current between the electrodes. Aluminum oxide is evidently a "non-conductor." The ζ -potential values which we report are of the same magnitude as theirs. From a consideration of the ζ -potential equation, it is evident that H must vary inversely as κ , the other terms remaining constant. Accordingly, the explanation for the large streaming potentials is merely that the aluminum oxide composing the diaphragm does not contribute appreciably to the conductivity of the system.

It is stressed that ζ -potential values obtained from determinations on diaphragm material which carries a large part of the total current in the cell are not thereby invalidated. However, it is evident from the data of Martin and Gortner that the use of cellulose in surface conductance determinations for liquids of specific conductivities less than 1×10^{-6} is inadvisable. Surface conductance is not appreciable in the case of liquids of large conductivities. Accordingly, it is evident that in surface conductance determinations, cellulose can be used only under limited conditions.

The ζ -potentials of the entire series of esters investigated, with the exception of ethyl formate, are negative (the sign applying to the aluminum oxide). The anomalous behavior of ethyl formate may be explained by assuming that it behaves not only as an ester but also as an "aldehyde." It is well known from the reactions of organic chemistry that the formates behave abnormally in respect to the other esters, and our results are in agreement with this fact. Not only is the sign of the charge reversed, indicating a reverse orientation of the dipoles, but the per cent of "unbalanced" oriented molecules is much greater indicating that the "aldehydic" group, with its secondary valencies, tends to promote a specific molecular orientation.

Figs. 3 and 4 show a slight but unmistakable effect of odd and even numbers of carbon atoms on the ζ -potential. A similar effect has been known for a long time in the case of some of the physical properties of the fatty acids, and it has led to the formulation of a zigzag structure for the carbon chain. This has been verified in a few cases by X-ray studies. Mueller¹³ has shown that this picture requires a difference in the packing at the ends of the molecules.

¹³ Proc. Roy. Soc., **124A**, 317-321 (1929).

In general, the electric moment of the double layer decreases with increasing length of the chain. The effect of alternate carbon atoms is felt in the case of this function also. For both series of esters, the "unbalanced" orientation of the molecules adsorbed at the interface decreases as the carbon chain increases in length. It should be stressed, however, that the calculations involved in the determination of the degree of orientation at the interface are based on the assumption that the distance between the centers of the charges at the interface are the same as between the dipoles of the molecule under the conditions of the dipole-moment determination. This may be far from the case, and accordingly the values must be interpreted with this in mind.

The data for the acids are not shown in a graph because of the question which is raised in the footnote to Table XVII as to the values for the constants for butyric acid. In general, however, the acid series shows similar trends to the ester series, excepting for the sign of the charge, which is positive for all of the acids and negative for all of the esters with the exception of ethyl formate. We do not believe that the anomalous behavior of ethyl formate is due to formic acid formed by hydrolysis, since special precautions were taken to ensure the purity of this ester.

The absence of a streaming potential at any pressure for either benzene or carbon tetrachloride indicates that the molecules of these compounds are entirely symmetrical. This confirms the earlier observations of Martin and Gortner³ who found that no streaming potential was produced at a benzene-cellulose interface, and those of Fairbrother and Balkin¹⁰ who observed no electro-endosmosis of benzene and carbon tetrachloride through a glass diaphragm.

Summary

The streaming potentials of aluminum oxide-liquid interfaces involving 15 pure organic liquids have been determined. The ζ -potential, the electric moment of the double layer, and the degree of orientation have been calculated. The data support the following conclusions:

1. The streaming potential increases linearly with the pressure, as is demanded by theory.
2. For a series of normal aliphatic esters, the ζ -potential and electric moment of the double layer decrease as the number of carbon atoms increases.
3. The "immobile" side of the double layer is negatively charged for all esters examined with the exception of ethyl formate (+), and positively charged for the series of n-aliphatic acids.
4. Ethyl formate behaves abnormally both as to sign and magnitude of the electrokinetic effect. This is probably due to the reactivity of the "aldehyde" group.
5. An alternating effect of the odd and even number of carbon atoms is observed on the ζ -potential and on the electric moment of the double layer.
6. The percent of "unbalanced" molecules oriented in the interface decreases with increasing length of the carbon chain.

7. The complete symmetry of the benzene and carbon tetrachloride molecules is evidenced by the lack of streaming potentials.

8. There is an almost exact parallelism between the electric moment per unit area of the double layer at the interface and the percentage of "un-balanced" oriented molecules in the interface. This observation leads to the conclusion that the electrokinetic forces at a solid-organic liquid interface are due to the electrical dissymmetry of oriented organic molecules and extends the molecular orientation, theory of Hardy, Harkins, Langmuir, Adam, *et al* to include surface electrical forces as well as surface tension and interfacial tension.

9. These studies confirm the suggestion of Martin and Gortner that streaming potential technic may be used to advantage in problems primarily concerned with the structure of organic molecules.

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A CORRELATION OF STREAM POTENTIALS AND SURFACE CONDUCTANCE

BY H. L. WHITE, FRANK URBAN AND E. A. VAN ATTA

At the 1931 Colloid Symposium we reported¹ that the stream potential of pyrex capillaries with 5×10^{-4} *N* KCl was independent of capillary size down to a bore of about 0.01 mm. Below this bore the potential decreased, being found about 75% as great with a 0.005 mm capillary as with large capillaries, *i.e.*, of 0.1 mm. McBain and Peaker² had found a specific surface conductance of 1.3×10^{-7} mhos at an interface of pyrex and 1×10^{-3} *N* KCl; by interpolation from their data we calculate that this would be not less than 1×10^{-7} mhos for 5×10^{-4} *N* KCl. If the mean conductance (resultant of volume and surface conductances) calculated on the basis of McBain and Peaker's data is put into the stream potential equation $E = \zeta PD/4\pi\eta\kappa$ the calculated stream potential for a 0.005 mm capillary with 5×10^{-4} *N* KCl would be only 8.4% of that with a large capillary in which surface conductance can be neglected. This discrepancy might have any one or all of three explanations, 1, that McBain and Peaker's surface conductance figures are too high, 2, that the classical stream potential equation does not hold in the smaller capillaries and/or, 3, that our previously reported stream potential figures for small capillaries are too high. We are now convinced that all three explanations hold.

First, we have shown^{3,4} that the specific surface conductance with pyrex and 5×10^{-4} *N* KCl is only 2.24×10^{-9} mhos, about 1/45 as great as found by McBain and Peaker. If the classical stream potential equation holds this conductance would make the stream potentials with 0.005 mm capillaries about 75 to 80% as great as with large capillaries, as we had found to be the case. This agreement seems to be a gratifying confirmation of our stream potential results on the smaller capillaries. We now recognize, however, that our figures of last year on stream potentials in the smaller capillaries are erroneous and that the apparent agreement is merely a coincidence. The error was due to our using a paper-paraffin condenser in the stream potential measurements. For the surface conductance work⁴ a standard condenser was essential. Stream potential determinations have been repeated on capillaries of various sizes using the standard 1 mf. mica condenser obtained since last year's report. It is found that the values for the larger capillaries, down to about 0.03 mm diameter, are correct as previously reported; below this bore the potentials fall off.

With the smaller capillaries the potentials are not only very much lower than with the larger, but much less satisfactorily reproducible. It had been

¹ White, Urban and Krick: *J. Phys. Chem.*, **36**, 120 (1932).

² McBain and Peaker: *J. Phys. Chem.*, **34**, 1033 (1930).

³ White, Van Atta and Van Atta: *J. Phys. Chem.*, **36**, 1364 (1932).

⁴ White, Urban and Van Atta: *J. Phys. Chem.*, **36**, 1371 (1932).

noted and reported last year that with the smaller capillaries reproducibility of results was much less satisfactory. This is now known to be due to residual charges on the paraffin condenser; the lack of reproducibility with the smaller capillaries as reported in the present paper is not due to any fault in the method of measurement but to actual changes in the capillaries. It has been found that the paraffin condenser gives the same readings as the mica with resistances up to about 10^9 ohms. With higher resistances the potential readings with the paraffin condenser are too high and variable due to variations in the amount of residual charge. With the mica condenser also the readings with the smaller capillaries vary from one experiment to another but consecutive readings agree. Even with the paraffin condenser consecutive readings may show excellent agreement, giving a false sense of security. Only after beginning to use the mica condenser and finding that a small capillary which might show a potential of 600 to 800 mv. with the paraffin condenser would at the same time show from 0 to 200 mv. with the mica did we realize that our earlier figures on small capillaries, with the paraffin condenser, are too high, although those on the large capillaries are correct. In Table I are shown a few stream potentials with the mica condenser.

TABLE I

Cap. no.	Length cm.	Diameter mm.	Stream potential mv./cm. Hg	
			2.5×10^{-4} N KCl	5×10^{-4} N KCl
58d	1.1	0.0964	31.4	15.4
59	4.66	0.0405	32.0	15.6
57a	1.97	0.039	31.0	
63a	0.25	0.0058	1.6	
60a	0.94	0.0055	5.8	
61	0.76	0.0053	0.0	
70a	0.13	0.0050	0.0	2.2
69a	0.34	0.0047	9.2	2.0

The stream potentials on the smaller capillaries are much lower than can be accounted for on the basis of the classical stream potential equation by the specific surface conductance of 2.24×10^{-9} mhos which we have found; they are rather of the magnitude expected if McBain and Peaker's values are correct. We thus have the paradoxical situation that with our surface conductance value the classical stream potential equation gives the stream potentials for small capillaries which we recorded last year but which are erroneously high, while the equation with McBain and Peaker's value for surface conductance gives stream potentials of about the value reported in this paper, which we believe to be correct. Since we can find no fault with our value for specific surface conductance we conclude that the classical equation does not hold in the smaller capillaries.

It must be pointed out that the validity of the low stream potential values for small capillaries reported here depends upon the assumption that these capillaries have been satisfactorily treated. We have exerted every possible effort as to cleanliness of water, alternating periods of evaporation and con-

densation during steaming, protection of capillary from dust, etc., to ensure that the state of the walls of these small capillaries is the same for a stream potential experiment as it is with the larger capillaries. Furthermore, we have found that a brief period of heating a large capillary in a Bunsen flame, after it has had hot water sucked through it for an hour, will usually give a stream potential about the same as that after steaming. When a small capillary is so heated it still shows the low stream potential value, just as after steaming. We must state, however, that we cannot have the same degree of conviction regarding the adequacy of the steaming treatment with the small capillaries as with the large. When, however, a number of treatments and determinations are carried out on a given capillary and in no case does the stream potential exceed 30% of that shown by a large capillary it seems probable that the low values are not purely fictitious.

Reichardt⁵ has attempted to develop an equation to express the influence of capillary diameter on the stream potential. His corrections do not bring the values down to those observed by us on the smaller capillaries. His equation $E' = E(1 + J_o/J_q)$ is equivalent merely to substituting for the bulk conductance the true conductance, *i.e.*, resultant of surface and bulk conductances, of the solution in the capillary. His correction for the departure from laminar flow suffered in the initial segment of a capillary reduces the stream potential in even a 0.005 mm capillary by only a few per cent. Thus, for a capillary of 0.005 mm diameter and 4 mm length his equation (17a), using a Reynolds number of 1000, gives $\chi_1 = 0.92$, *i.e.*, the stream potential would be lowered by only 8% due to this factor. We are not yet in a position to present a theoretical treatment of our stream potential values on the smaller capillaries.

Briggs⁶ has pointed out that surface conductance may vary independently of zeta potential and has concluded that surface conductance is therefore not ionic conductance. He suggests that the effects of salts upon surface conductance are a function of their effects upon the equilibrium between monohydrol and polyhydrols. The former is supposed to be an electronic conductor; varying the nature or the concentration of ions affects surface conductance by affecting the concentration of monohydrol in the double layer. Briggs finds that the surface conductance with the tri and tetravalent cations, Al^{+++} and Th^{++++} , after passing through a maximum falls off with increasing concentration. This is attributed to their decreasing the concentration of monohydrol. Urban and Daniels⁷ have found, however, that bivalent cations decrease the partial specific heat of water more than do monovalent cations. The presumption is that the effect would be still more marked with tri and tetravalent cations. A decrease in specific heat indicates, *inter alia*, a decrease in polyhydrol concentration. This finding speaks against Briggs' view that polyvalent ions reduce the monohydrol concentration.

With KCl Briggs found that surface conductance increased continuously with concentration while zeta passed through a maximum and then fell off

⁵ Z. physik. Chem., **154**, 337 (1931).

⁶ Colloid Symposium Monograph, **6**, 41 (1928).

⁷ Urban: J. Phys. Chem., **36**, 1108 (1932)

continuously. This lack of correlation, as well as the findings with polyvalent ions, led him to the statement that surface conductance is not a function of the zeta potential. The thesis developed in the present and the accompanying paper is that surface conductance is a function of zeta in the following sense, that a correlation between surface conductance and zeta exists only provided that the essential conditions for exhibiting a normal zeta potential are established. In the case of glass capillaries, with the stream potential taken as an index of zeta, this means that the capillary must be of at least 0.016 to 0.02 mm. diameter and must have been subjected to a standardized treatment such that a maximum stream potential is developed.⁸ If a capillary of proper size is so treated it will show with $5 \times 10^{-4} N$ KCl a stream potential corresponding to a zeta potential of about 120 mv. and a specific surface conductance of about 2.24×10^{-9} mhos. If the capillary is allowed to stand in the solution for several days or if it is used without having been first treated it will show a much lower zeta potential, which may drop even to zero, with practically no change in surface conductance. This looks like a failure of correlation between surface conductance and zeta potential. If, however, a normal zeta potential is established, the charge density calculated from this and the surface conductance calculated from the charge density, assuming normal viscosity, mobility and dielectric constant, the surface conductance so calculated agrees with the observed. We have interpreted these facts as meaning that with the untreated capillary the diffuse layer is absent or reduced while with the treated capillary the initially existing diffuse layer gradually collapses into the Helmholtz layer. The sum of the charges in the entire double layer remains constant; the ions in the Helmholtz layer can conduct electrical current but cannot contribute to stream potential, *i.e.*, they can move in an electric field but not under hydrostatic pressure. The surface conductance is, therefore, unaffected by the distribution ratio of ions between diffuse and Helmholtz layers, but the zeta potential depends upon this distribution. If we establish the proper conditions practically all of the cations at a glass-aqueous interface are in the diffuse layer with concentrations of KCl not greater than $10^{-3} N$. When a normal, *i.e.*, maximum for that system, zeta potential exists the cation conductance in the diffuse layer (with concentrations of KCl not greater than $10^{-3} N$) is therefore practically equivalent to the total cation conductance and can be calculated from the zeta potential.

With increasing concentration, where it is no longer true that practically all of the cations are in the diffuse layer, one can still calculate surface conductance from normal, *i.e.*, maximum for that system, zeta potentials if the distribution of cations between diffuse and Helmholtz layers is first calculated

⁸ The determination of both surface conductance and stream potential on one and same capillary is difficult but not impossible. The percentage of error is rather large since, if a capillary of diameter greater than 0.02 mm is used the ratio of surface to volume is too low for the most accurate determinations of surface conductance while if the diameter is less than 0.016 mm the stream potential is likely to be too low. Numerous determinations on a capillary of 0.0186 mm diameter have shown marked fluctuations in stream potential depending upon its treatment, while the surface conductance remained constant. Furthermore, the type of treatment known to be essential to the establishment of a normal stream potential in large capillaries is known not to be essential to the maintenance of a constant surface conductance in small capillaries.

according to the method outlined in the accompanying paper, and allowance made for the conductance of ions which are no longer in the diffuse layer.

While affording a satisfactory explanation of both Briggs' and our results with monovalent cations this concept at first thought seems inadequate to account for Briggs' finding that with polyvalent cations the surface conductance progressively decreases as concentration and zeta potential increase. We are not yet ready to discuss this situation fully. Insufficient knowledge of the work functions of adsorption of these ions makes it impossible to calculate satisfactorily the distribution between the diffuse and the Helmholtz layers. Until such calculations are possible we cannot judge of the applicability of our equations to the case of polyvalent cations. We may point out that McBain and Peaker, working with pyrex surfaces, did not find a decrease in surface conductance on increasing the concentration of AlCl_3 , as did Briggs with a cellulose diaphragm. They found that the increase in conductance on increase of concentration was even greater with AlCl_3 than with KCl . Furthermore, Bull and Gortner⁹ working with cellulose diaphragms found with ThCl_4 a fall in surface conductance followed by a rise, within the same range of concentrations used by Briggs. We are now investigating the surface conductances at pyrex surfaces of various concentrations of salts with ions of different valences but are not yet prepared to report our findings.

Summary

1. The stream potentials with capillaries of 0.005 mm diameter are from 0 to 25% as great as with large capillaries, instead of 75 to 85% as great, as was reported last year.

2. These low figures cannot be accounted for by the classical stream potential equation or by any modification so far proposed. The possibility that unavoidable inadequacies of treatment of the smaller capillaries may be in part responsible for these abnormally low values cannot be excluded but it is believed that the low values are not entirely fictitious.

3. A necessary and sufficient condition to a correlation between surface conductance and stream potentials is that the conditions essential to the exhibition of a normal stream potential be established. The zeta potential may fluctuate with no change in surface conductance but if a normal zeta is established surface conductance can be calculated from it and vice versa.

4. Briggs' findings on monovalent cations which led him to the conclusion that surface conductance is not a function of the zeta potential can be interpreted as indicating that in his experiments the diffuse layer is less pronounced and varies more with concentration than is the case at glass surfaces; under these conditions the zeta potential is not an index of the charge density until the distribution of charges between the components of the double layer is determined. The case of polyvalent cations is being further investigated.

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⁹ J. Phys. Chem., 35, 307 (1931).

APPLICATION OF THE DOUBLE LAYER THEORY OF OTTO STERN. I

BY FRANK URBAN AND H. L. WHITE

In recent communications, surface conductance and stream potential measurements in Pyrex capillaries of various sizes were reported.¹ Capillaries of from 0.00182 to 0.10 mm bore were used, macroscopic surface to volume ratios as high as 22,000 to 1 being obtained as compared with 1600 to 1 by McBain, Peaker and King.² A specific surface conductance for Pyrex glass and 0.0005 *N* KCl of 2.24×10^{-9} mhos was found, as compared with an extrapolated value of 1×10^{-7} by McBain and Peaker, their figure being 45 times as great as ours. If, as we believe, McBain and Peaker's figures for surface conductance are erroneously high, McBain's arguments against the ζ -potential concept lose their weight.³

A further confirmation of the ϵ - ζ -potential concept of Freundlich would result, if it could be shown that there is a quantitative correlation between surface conductance and ζ - and ϵ -potentials, respectively. In the present paper, it will be shown that surface conductance and ζ -potential are related. The second relation, namely between ϵ -potential and surface conductance, will be dealt with in a subsequent publication.

In order that ζ -potential values calculated from surface conductance might be compared with those obtained by a second independent method, we selected the stream potential technique. ζ -potentials calculated from stream potentials are in agreement with the Helmholtz theory, providing the capillary radius is approximately $\geq 10 \mu$ and that Poiseuille's law is obeyed. This view is based on our experimental findings.⁴ As the Helmholtz equation breaks down below a capillary radius of about 10μ , it follows that in this region it is not permissible to calculate absolute values of ζ -potential or electric moment by means of this equation.

Double Layer Equation of Otto Stern⁵

The theoretical bridge between surface conductance and ζ -potential is to be found in Stern's equation which describes the structure of an electrical double layer due to ionic adsorption at phase boundaries. It represents a synthesis of the Helmholtz and Gouy double layer concepts.⁶ According to this equation:

¹ White, Urban and Krick: *J. Phys. Chem.*, **36**, 120 (1932); White, Van Atta and Van Atta: **36**, 1364 (1932); **36**, 1371 (1932).

² *J. Am. Chem. Soc.*, **51**, 3294 (1929).

³ *J. Phys. Chem.*, **34**, 1033 (1930).

⁴ *Loc. cit.*

⁵ *Z. Elektrochemie*, **30**, 508 (1924).

⁶ For a discussion of the equation, see Buzagh: *Kolloid-Z.*, **52**, 57 (1930); Freundlich: "*Kapillarchemie*," **1**, (1930); Mueller: *Kolloidchem. Beihefte*, **26**, 257 (1928); Langelaan: *Arch. néerland. Physiol.*, **16**, 145 (1931) (in English).

$$\begin{aligned}
 (1) \quad \underbrace{K_0 (\psi_0 - \psi_1)}_{\eta_0} = & \underbrace{FZ \left\{ \frac{1}{1 + \frac{1}{18c} e^{\frac{\Phi_+ - F\psi_1}{RT}}} - \frac{1}{1 + \frac{1}{18c} e^{\frac{\Phi_- + F\psi_1}{RT}}} \right\}}_{\eta_1} + \\
 & \underbrace{\sqrt{\frac{DRTc}{2\pi}} \left\{ e^{\frac{F\psi_1}{2RT}} - e^{\frac{-F\psi_1}{2RT}} \right\}}_{\eta_2}
 \end{aligned}$$

Where N Avogadro number; e charge of electron; K_0 capacity of Helmholtz condenser; ψ_0 potential drop across Stern double layer; ψ_1 potential drop across diffuse (Gouy) double layer, approximately equal to ζ -potential; η_0 excess negative charges on solid surface; F 96,500 coulombs; Z maximum number of mols of ions which can be accommodated in a unimolecular layer of 1 cm². (max. no. of ions = z); Φ_- molar energy of adsorption of anions; Φ_+ molar energy of adsorption of cations; c concentration of salt in mols per cm³; η_1 excess positive charges in Helmholtz layer; η_2 excess positive charges in diffuse layer; D dielectric constant; l_a mobility of anion; l_k mobility of cation; η_0 number of anions in inner Helmholtz layer, if the cations can be neglected.

Distribution of ions in Helmholtz and Gouy Layers.

For 5×10^{-4} M KCl/liter and Pyrex Glass

From Equation (1), it follows that

$$(2) \quad \text{Number of cations in outer Helmholtz layer} = \frac{z}{1 + \frac{1}{18c} e^{\frac{\Phi_+ - F\psi_1}{RT}}}$$

$$(3) \quad \text{Number of anions in outer Helmholtz layer} = \frac{z}{1 + \frac{1}{18c} e^{\frac{\Phi_- + F\psi_1}{RT}}}$$

$$(4) \quad \text{Number of cations in Gouy layer} = \sqrt{\frac{DRTc}{2\pi e^2}} \cdot e^{\frac{F\psi_1}{2RT}}$$

$$(5) \quad \text{Number of anions in Gouy layer} = \sqrt{\frac{DRTc}{2\pi e^2}} \cdot e^{\frac{-F\psi_1}{2RT}}$$

The ratio of anions to cations in the inner Helmholtz layer is perhaps of the order of e^{Φ_+}/e^{Φ_-} .

In order to simplify the calculations, the cations in the inner Helmholtz layer, also the ions of (2), (3), and (5) can be neglected. Equation (1) reduces in that case to

$$(6) \quad \eta_0 = \sqrt{\frac{DRTc}{2\pi e^2}} \cdot e^{\frac{-F\zeta}{2RT}}, \text{ and, therefore}$$

$$(7) \quad \text{Surface conductance/cm}^2 = \sqrt{\frac{DRTc}{2\pi e^2 N^2}} \cdot e^{\frac{-F\zeta}{2RT}} (l_a + l_k).$$

Equation (7) implies that anions as well as cations are mobile. This assumption is in conflict with the well-known electrosmose equation, where it is assumed that the ions of the inner Helmholtz layer are fixed.

It will now be shown that the simplification leading to (7) is permissible. (4) and (5) will be evaluated first. The only unknown in these equations is ζ ($\cong \psi_1$) which can be calculated from stream potentials. The average stream potential observed by Lachs and Biczky⁷ (by interpolation) with 5×10^{-4} M KCl was 16.4 mv/cm Hg; that observed by White, Urban and Krick for large capillaries, was 17 mv/cm Hg. Taking the average of these two sets of data we get 16.7 mv/cm Hg. Average temperature is taken as 22°C. Since for large capillaries, no size corrections are necessary, the calculation for ζ is made by the Helmholtz equation.⁸

$$(8) \quad \zeta = \frac{1.67 \times 10^{-2} \times 3.1416 \times 10^{-2} \times 7 \times 10^{-5} \times 9 \times 10^{11}}{13.6 \times 981 \times 80} = 0.124 \text{ v.}$$

Since we are here operating only in the diffuse layer, the normal value of 80 for D is used.⁹ The number of cations in the Gouy layer, according to (4), equals

$$(9) \quad \sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^7 \times 295 \times 5 \times 10^{-7}}{2 \times 3.1416 \times 2.27 \times 10^{-19}}} \times \frac{9.65 \times 10^4 \times 3 \times 10^8 \times 1.24 \times 10^{-1}}{e \cdot 3 \times 10^2 \times 2 \times 1.99 \times 4.183 \times 10^7 \times 2.95} = 0.96 \times 10^{13}.$$

while the number of anions, according to (5) is 0.73×10^{11} . Hence (5) can be neglected.

The evaluation of (2) and (3) requires a knowledge of z and Φ_+ , Φ_- . We shall use 1.27×10^{15} for z , obtained from KCl crystal lattice measurements. As pointed out by Stern, Φ_+ and Φ_- can be calculated from $c_m = 2.3 \times 10^{-4}$ M KCl per liter, the concentration at which $\zeta = 0.140$ v is a maximum (data of Lachs). The result of the calculation is

$$(10) \quad \Phi_+ = 1.34 \times 10^{11}$$

$$(11) \quad \Phi_- = -1.37 \times 10^{11}$$

Substituting these values in (2), the number of cations in the outer Helmholtz layer is found to be

$$(12) \quad 5.8 \times 10^8 = \frac{1.27 \times 10^{15}}{1 + \frac{1}{9 \times 10^{-6}} \cdot e^{\frac{3 \times 10^2 \times 1.34 \times 10^{11} - 9.65 \times 10^4 \times 3 \times 10^8 \times 1.24 \times 10^{-1}}{3 \times 10^2 \times 1.99 \times 4.183 \times 10^7 \times 2.95 \times 10^2}}}$$

The number of anions per cm², according to (3), is

$$(13) \quad 3.1 \times 10^{10} = \frac{1.27 \times 10^{15}}{1 + \frac{1}{9 \times 10^{-6}} \cdot e^{\frac{-3 \times 10^2 \times 1.37 \times 10^{11} + 9.65 \times 10^4 \times 3 \times 10^8 \times 1.24 \times 10^{-1}}{3 \times 10^2 \times 1.99 \times 4.183 \times 10^7 \times 2.95 \times 10^2}}}$$

(12) and (13) are negligible.

⁷ Z. physik. Chem., **148** A, 441 (1930).

⁸ The Helmholtz stream potential equation does not conflict with Stern's double layer structure, if ζ is defined as the potential of the diffuse layer.

⁹ Deubner: Ann. Physik, **84**, 429 (1927), cited in Handbuch der Physik, XIII, 372 (1928); Kallmann and Doch: Z. physik. Chem., **126** A, 305 (1927).

Finally, the ratio of anions to cations in the inner Helmholtz layer being of the order e^{Φ_+}/e^{Φ_-} , we obtain by substitution

$$(14) \quad \frac{\text{anions}}{\text{cations}} = \frac{e^{2.71 \times 10^{11}}}{1}$$

These preliminary calculations indicate that the simplifications leading up to Equation (7) are permissible. Before putting (7) to the test, two important points will have to be discussed.

(a). The objection may be raised that the true surface of the capillaries is not known, and that it is the micro-surface which determines conductivity. A macro-surface of 1 cm² might perhaps, let us say, represent a micro-surface of several cm.² It can be readily seen, however, that a *hap-hazard* micro-structure such as may be presumed to exist in the case of glass would leave the surface conductance unchanged.

(b). The preliminary calculations indicated that for 5×10^{-4} M KCl per liter $\eta_1 \ll \eta_2$. This is the exact opposite of the assumption made by Stern, namely, $\eta_2 \ll \eta_1$, on which he based his method of calculating Φ_+ and Φ_- . Our values of Φ_+ and Φ_- , which have been calculated according to Stern, can therefore be but a rough approximation. Nevertheless, allowance for a large error in the calculated Φ_+ and Φ_- values does not materially change the relation $\eta_1 \ll \eta_2$.

Calculation of Surface conductance for 5×10^{-4} M KCl per liter, by (7).

$$(15) \quad \text{Surface conductance/cm}^2 =$$

$$\sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^7 \times 295 \times 5 \times 10^{-7}}{2\pi \times 4.774^2 \times 10^{-20} \times 6.062 \times 10^{46}}} \cdot e^{\frac{-0.65 \times 10^4 \times 0.124}{3 \times 10^3 \times 2 \times 1.99 \times 4.183 \times 10^7 \times 295}} \cdot 150.$$

$$(16) \quad \text{Surface conductance/cm}^2 = 2.4 \times 10^{-9} \text{ mho.}$$

The experimentally observed surface conductance is 2.24×10^{-9} mho.

The normal value of 75 for the mobility of Cl⁻ and K⁺ was substituted in (15).

Calculation of ζ from surface conductance. 2.5×10^{-4} M KCl per liter.

We find experimentally that

$$(17) \quad \text{Surface conductance/cm}^2 = 1.35 \times 10^{-9} =$$

$$\sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^7 \times 298 \times 2.5 \times 10^{-7}}{2\pi \times 2.27 \times 10^{-17} \times 3.67 \times 10^{47}}} \cdot e^{\frac{0.65 \times 10^4 \times 3 \times 10^3 \times \zeta}{2 \times 1.99 \times 4.183 \times 10^7 \times 295}} \cdot 150$$

$$(18) \quad \zeta = \frac{0.96 \times 3 \times 10^2}{2.5 \times 10^3} = 0.11 \text{ v.}$$

The value determined from stream potential is $\zeta = 0.12$ v. This agreement is satisfactory.

Similar calculations with 10^{-5} M KCl per liter, 10^{-4} M and 10^{-3} M have been undertaken. The agreement was as good as could be expected. The

data have not been included in this paper, as a greater number of surface conductance determinations in solutions of the last mentioned concentrations have yet to be carried out.

Discussion

The good agreement between our calculated and observed quantities appears to justify the underlying assumptions:

- (a). In an electric field, *all* ions of the double layer are mobile.
- (b). The mobility of the double layer ions is close to normal.
- (c). The double layer at a Pyrex/KCl-solution interface is composed of K^+ and Cl^- .
- (d). The number of cations in the inner Helmholtz layer is negligible, at the KCl concentrations investigated.

The assumption of Helmholtz and von Smoluchowski that the ions on the wall (ions of the inner Helmholtz layer) are immobile, would give a calculated value of surface conductance one-half of that observed. In order to overcome this difficulty, the abnormally high mobility of 150 for K^+ would have to be postulated (as compared to a normal value of 75). It is undoubtedly less forced to attribute normal mobilities to K^+ and Cl^- and to allow both to move. At the present time, it is an open question as to how much energy is required for lateral motion of an ion along a surface.¹⁰

By assigning normal mobilities to both K^+ and Cl^- , the observed surface conductances harmonize with the calculated ones. This could be the case only if the double layer contained but insignificant numbers of ions other than K^+ and Cl^- .

In order to test these assumptions still further, we are determining surface conductance with other salts. Assumption (c) can be tested directly, by obtaining adsorption isotherms on Pyrex glass wool. These should also make it possible to evaluate (d).

Finally, we conclude, on the basis of the evidence presented in this paper, that Stern's concept of a variable charge governed by adsorption, is sound.

Summary

1. It has been shown that in dilute solutions ζ -potential and surface conductance are related.
2. Evidence has been adduced to show that the ions of the inner Helmholtz layer are mobile, and also
3. That the assumption $\eta_1 \gg \eta_2$ in dilute solutions made by Stern for the purpose of calculating Φ_+ and Φ_- is not justified.¹¹

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¹⁰ Private communication from Dr. Henry Eyring, Princeton.

¹¹ Hans Müller has raised the same objection independently. *Kolloidchem. Beihefte*, 26, 282 (1928).

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. VI'

BY WILDER D. BANCROFT AND JOHN E. RUTZLER, JR.**

In previous papers comprising this series, it was shown that peptizing agents, sodium rhodanate in particular, reverse the agglomeration brought about by anesthetics and allied drugs. Human beings, dogs, rabbits, and plants, have been made to recover experimentally from anesthetics or hypnotics more quickly by the administration of a peptizing agent, given in order to counteract the agglomeration which is a part of the induced condition. To date, despite a great many ill-founded criticisms and a few badly planned experiments, the theory of reversible agglomeration stands forth as the only rational conception of the action of many drugs. Experimental support of the theory continues to come in from those who understand how to make use of a good theory. In order to secure further support of the theory that anesthesia is accompanied by reversible agglomeration of certain protein colloids of the central nervous system, experiments were carried out on goldfish, *Carassius auratus*. The limited facilities of a chemical laboratory for physiological research still enable one to perform a good many experiments with goldfish. However, no attempt was made to reach the magic number of experiments—one hundred.

At first sight, it may seem that the goldfish is structurally a simple animal upon which to experiment. Because this was not found to be the case, it seems wise to consider briefly some of the major facts of the neuro-anatomy of fishes.

Kyle¹ says: "The spinal nerves connected with the different segments are arranged in the same way as in Higher Vertebrates and there is also an internal sympathetic system. The cranial nerves are for the most part the same, with some variations in their development and importance. The VIIIth nerve, for example, is specially large and is connected with an independent centre in the medulla, the tuber acusticum. This is supplied from the general cutaneous nerves, lateral line system, as well as from the auditory organ or statocyst."

On page 159: "The simplest form of sense organ is seen in the end-buds which occur anywhere on the skin of fishes. On Higher Vertebrates these become restricted to the mouth as taste-buds. Sometimes they are raised on eminences, but most often they sink deeper into the skin and the nerve-endings become embedded in mucus or glandular tissue. Whether they are all connected with reception only, we do not know. . . ." In another place,

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** Eli Lilly Research Fellow.

¹ "The Biology of Fishes," 167 (1926).

Kyle says that the diffuse end-buds seem to be able to detect differences in the chemical nature of the surroundings.

On page 160 he says: "On the other hand the organs of the lateral line have quite a different function. . . . According to Parker these organs are not stimulated by light, heat, salinity of water, food, oxygen, carbonic acid, water pressure, currents, or sound. . . ."

"The lateral line organs seem also to be of some use both in orientation, according to the different strengths of currents on the two sides of the body, and in balancing. He found that when the pectoral and ventral fins were removed, the fish (*Opsanus*) showed no lack of equilibrium so long as the lateral line was left intact."

On page 141 Kyle says: "So long as a fish is alive, its internal constitution and particularly the composition of its blood are quite different from those of the surrounding medium. It is self-contained and only takes in the materials it wants to take in. . . ."

"Freshwater fishes like the Carp have a much greater [osmotic] pressure within the blood than that externally; by increasing the amount of salt in the water to 10 grm. *pro mille* Portier and Duval were able to obtain equilibrium within and without; but with still further increase in the salinity the gill membrane seemed to be forced and the fish died. As the pressure of the blood also increased, though slightly, in these experiments, it would seem that a small amount of the external salts in solution is able to pass through the membrane. But this is by no means certain; and other observers think that only water is able to pass through. It is possible that the fish is able to withdraw water and salts from the tissues and thus regulate its exchanges. The Salmon, for example, does not change its osmotic pressure all at once on entering fresh water; and the Eel, when transferred from fresh to salt water, does not assume the osmotic pressure of the latter."

On page 18 we find: "But the latter organs [the kidneys] are not so well-developed in the fishes as in higher vertebrates, and thus the guanin and lime become deposited in the dermis . . . and in common with guanin lime is often present in the internal tissues of the fish, as in the retina of the eye, peritoneum, air-bladder, etc. . . ."

From these few quotations it can be seen readily that exposing fish to electrolytes and anesthetics may give rise to several phenomena, other than straightforward anesthesia and recovery. It was found almost at the outset that the problem was not simple.

In order to make sure that in the case of the fish we are dealing with protein colloids of the nervous system which respond to the electrolytes of the lyotropic series like those of the other animals with which we have dealt, swelling experiments were performed.¹ Whole, freshly excised, goldfish brains were weighed and then placed in ten percent solutions of sodium iodide, sodium chloride, and sodium citrate. After being in the solutions for periods of one, two, and twenty hours each of the brains was again weighed. From these data the percentage change in weight was computed. A positive change in weight

¹ The authors are grateful to Dr. Robert L. Nugent for performing these experiments.

was found in the case of sodium iodide and sodium chloride, the sodium iodide causing a much greater increase in weight than the sodium chloride. In the sodium citrate solution the goldfish brain lost weight. This was found to be the case whether the hydrogen ion concentration of the sodium citrate solution was barely on the acid or on the alkaline side of the neutral point. So, sodium iodide and sodium chloride peptize goldfish brains, as they should; and sodium citrate produces agglomeration. The observed relations of the size of the different specimens bore out the swelling data, i.e., those that swelled most were largest in size.

Dr. Nugent also experimented with the electrophoresis of thoroughly macerated goldfish brains which had been washed and suspended in a buffer solution having an hydrogen ion concentration of $1 \times 10^{-6.5}$. All of the particles that were observed travelled quite rapidly toward the anode, showing that they were strongly negatively charged. This indicates that their isoelectric points were well below $[H^+] = 1 \times 10^{-6.5}$.

In performing experiments on live fish care was always taken to have the water containing the different compounds being studied at the temperature of the room. Thus, none of the observed effects was due to temperature differences. Apparently healthy fish were always used. When more than one experiment was done on a single fish, at least a week's time was allowed to elapse between the experiments. Generally, fish of approximately equal size were used. At least one check experiment was almost always performed; and sometimes many check experiments were made. The fish were not experimented upon shortly after being fed.

The first experiments were performed using amytal as the anesthetic. The anesthetic was prepared by warming an excess of sodium bicarbonate with three grams of amytal and fifty cc of distilled water. This was then diluted to two liters with tap water, and the solution filtered. The filtered solution was used as the anesthetic bath. Six goldfish were placed in this bath. One was anesthetized in fourteen minutes; and five lost consciousness in fifteen minutes. In each anesthesia experiment reported in this paper, unless otherwise stated, the fish was considered to be anesthetized when all voluntary movement ceased, and when there was no visible response to touch, a glass rod being used for testing the latter. As with mammals, it was observed that the fish passed through a stage of stimulation prior to the loss of consciousness. When, later, the effect of other anesthetics is described it will be seen that the period of excitation brought about by amytal is short, of the order of five minutes. Further, the period of stimulation can be varied greatly by changing the concentration of the anesthetic. Two of the anesthetized fish were placed in a 2% solution of sodium citrate which was made just acid to litmus paper with citric acid; two were put in tap water to be used as controls; and two were put into a 2% solution of sodium rhodanate.

The fish that were put into the sodium citrate laid on their sides, their tails extended below the line of their bodies. This is in marked contrast to their behavior in the anesthetic bath in which there was only a slight loss of normal balance. After a period of five to ten minutes the fish in the sodium

citrate solution underwent what appeared to be a convulsive phenomenon; their bodies began to jerk. This did not result in propulsion through the water. These movements stopped in less than five minutes and the fish began to swim around excitedly. When left long in such a sodium citrate solution, after apparent recovery, the fish finally became more quiet than a normal fish. When the fish were transferred from the sodium citrate solution to tap water while still excited, a period of wild excitement ensued; they broke through and cleared the surface of the water so that their bodies were entirely out of water. This period of excessive excitement lasted for about fifteen seconds. The fish then lapsed back into a fairly deep narcosis during which they were balanced normally, and the rate of respiration became very low. At this stage when the fish were left in the tap water in other experiments they remained narcotized for upwards of forty-five minutes. On the other hand when they were put back into the sodium citrate solution until they became excited again, and then transferred to the water once more, and the whole process repeated several times, it was found that the fish recovered from the effects of the anesthetic more quickly than if they were only put into tap water after being narcotized. These results can be obtained most readily by preparing the anesthetic bath in the following manner. Mix one gram of amytal with one gram of sodium bicarbonate in about 50 cc. of water. Warm to about 60° and dilute to 560 cc. Adjust the pH to 9.05 - 9.4; then filter. The sodium citrate solution is best prepared by adding 18 grams of acid sodium citrate to one liter of water. Then add concentrated sodium hydroxide until the pH equals 6.0.

At the time when the fish that were treated with sodium citrate recovered, the controls were still very deeply narcotized, more deeply, in fact, than when they were removed from the anesthetic bath. They were finally brought out of the anesthesia by treating them with sodium citrate.

The fish that were placed in the two percent sodium rhodanate solution did not recover very rapidly; so they were treated with sodium citrate. However, it was noticed that while in the sodium rhodanate solution the respiration of these fish was more even and rapid than that of those in sodium citrate or tap water. Further, the fish in the sodium rhodanate solution suffered no loss of balance; they stayed on the bottom of the bowl, whereas those in the sodium citrate solution floated.

At first sight, it would seem from these results that sodium citrate arouses the fish from amytal anesthesia more quickly than plain tap water. Therefore it was decided to trace the phenomenon down. Two fish were left in a 2% solution of sodium citrate for three minutes; they became hyperexcitable. The fish were then transferred to tap water in which they became slightly depressed following hyperexcitability; they stayed in tap water for five minutes. After that the fish were put into the sodium citrate solution again for a period of three minutes; again they became extraordinarily excited in this solution. Upon being replaced in tap water they became slightly more hyperexcitable; this was followed by a slight depression. The fish were left in the tap water for 21 minutes following which they were placed in the sodium citrate for two and one-half minutes. Again, the cycle, hyperexcitability→depression→normal,

was observed. The sodium citrate solution was at $[H^+] = 1 \times 10^{-6.45}$. The whole experiment was repeated several times with slight variations. In each case the result was qualitatively the same. The fish still behaved qualitatively the same when the solution was adjusted to $[H^+] = 1 \times 10^{-6.1}$ and $1 \times 10^{-7.1}$. It was observed that while in the sodium citrate solution the fish breathed spasmodically, so that they appeared to be holding their breath. It was found that a four percent solution of sodium citrate killed fish in an hour or less. So, most of the phenomena of rousing a fish from amytal anesthesia were duplicated, though in a much less striking manner, by the use of sodium citrate and unanesthetized fish.

It does not seem probable that the sodium citrate acts upon the same centers as the amytal in the above experiments. An experiment was performed which lends a great deal of credence to that idea. Two fish were anesthetized in an amytal solution. Then they were placed in an extremely dilute solution of sodium sulphate. Two aluminum electrodes were connected to a source of electricity which delivered five volts. When the fish were touched by the electrodes they were stimulated to activity. The stimulation ceased when the contact was broken. The same result was observed four or five times. This did not cause the fish to awaken truly from the narcosis. Likewise, fish anesthetized by urethane were brought out of the anesthesia more rapidly than controls by shocking them, using four volts. There is no evident reason why electric shocks should peptize the protein colloids of the nervous system of the fish.

Another fact of importance is that after allowing four or five fish to remain in a sodium citrate solution long enough to recover apparently from anesthesia, the solution becomes cloudy. In about a day the sol coagulates. This is coagulated fish slime. Likewise sodium amytal appears to do the same thing to a lesser degree. A 10% solution of sodium rhodanate will do the same thing by another mechanism in a longer time. The tearing off of the adherent slime must affect the fish.

From these data it appears quite certain that the apparent recovery brought about by sodium citrate is not due to a peptizing action upon the same substrate as that which is agglomerated by the amytal. As the theory stands, sodium citrate acts in one or both of the following ways: by the precipitation of calcium salts on the outside, and perhaps inside of the fish, thus causing stimulation; by the tearing off of the slimy coating and slight agglomeration in the skin sense-organs.

It will be evident from what follows that in some cases the important thing is the precipitation of calcium salts; and in others it is the agglomeration in the skin sense-organs and tearing off of the slimy coating.

Experiments with ether were undertaken next. In the first experiment 5.4 cc of anhydrous ether were dissolved in 1.5 liters of tap water. Two fish were placed in this solution. After eight minutes they began to swim backwards. They continued to do this for 10-15 minutes. Forty minutes after the fish were put into this solution four cc more ether were added. The bowl was kept covered during the experiment. The fish were left in the solution for

another twenty minutes when all noticeable gill and mouth movements ceased. One was placed in a 2% solution of sodium citrate that was just acid to litmus; and the other was put into a 2% solution of sodium rhodanate. Both recovered at the same time. The fish were re-anesthetized in the ether solution about ten minutes later; this time they went under in five minutes. This result permits of the conclusion either that the ether was not all out of the fish at the time that they were re-anesthetized, or that the agglomeration brought about by the ether was not entirely reversed.

From the above and several other comparable experiments in which ether was used as the anesthetic an interesting comparison with the anesthesia produced by sodium amytal can be made. Ether anesthesia, under the conditions of the experiment, has a much longer induction period. While the narcosis produced by ether appears to be deep, it does not last nearly so long as the amytal anesthesia. From the results of several experiments it appears that the fish recover from ether anesthesia in tap water in from two to four minutes; while the recovery time from amytal is of the order of one hour. When the fish are removed from the anesthetic bath and put into tap water the anesthesia appears to become deeper in the case of amytal, and lighter in the case of ether. This merely indicates that ether leaves the fish more rapidly than amytal. While making this comparison it is of interest to note that in several attempts to anesthetize fish with alcohol failure resulted. Solutions containing 1-3% of alcohol were used. In each case there was a long period of excitation, 45 minutes to two hours being required to produce anesthesia. During most of this time the fish were stimulated and swam around in an intoxicated manner. The elapsed time between the onset of depression and deep narcosis was very short in comparison to the long period of stimulation. In all of the experiments that were performed with alcohol as the anesthetic, the narcosis produced was deadly; very few fish survived alcohol narcosis. However, if the treatment was discontinued just short of the narcosis stage and the fish placed in tap water, they recovered exceedingly rapidly.

Nembutal, an anesthetic of the barbituric acid series was used in several experiments. It is closely related to amytal, but acted somewhat differently from amytal in the experiments that were conducted. In the course of exhaustive experiments on sodium amytal it was found that the pure salt when dissolved in water was toxic to the fish. Likewise nembutal, which is also a sodium salt, proved to be quite toxic to goldfish. In a 0.14% solution of nembutal it required on an average of 49 minutes to produce anesthesia. A very long period of great depression was noted before the anesthetic stage came on. Narcotized fish placed in a 2% sodium citrate solution behaved qualitatively the same as they did under amytal anesthesia. Quantitatively, they were stimulated more quickly by the sodium citrate than the fish anesthetized with amytal as previously described; the whole phenomenon of stimulation by sodium citrate was less marked. The narcosis induced by nembutal did not appear to be so deep as that induced by amytal.

While comparing different anesthetics, it is of interest to include urethane. Urethane dissolved in water to make a 0.5% solution or a 0.75% solution

anesthetizes goldfish in from seven to fifteen minutes. In almost every case the tail goes out of commission as a swimming help first. Then, as a result of incoordinated movements of the pectoral fins, the fish swim backwards slowly. A period of slight stimulation is noticed prior to the onset of unconsciousness. The fish do not lose their balance entirely in any of the anesthetic solutions, as they do in sodium citrate. Recovery in tap water from urethane anesthesia requires approximately nine to fifteen minutes. The anesthesia does not appear to be very profound; but the effect is more lasting than that of ether. The toxicity of urethane is low. In one case a fish was left in the anesthetic bath for twenty minutes after voluntary movements had ceased and tactile stimulation evoked no response. Yet the fish recovered in a 2% solution of sodium citrate just as rapidly as another fish that remained in the bath only four minutes after the induction of anesthesia. The concentration of urethane in the solution affects very greatly the time required to produce anesthesia. For instance, two fish were not anesthetized in twenty minutes in a 0.2% solution of urethane; while a 3.5% solution brings about a good narcosis in less than two minutes. Large goldfish are more resistant to anesthesia by urethane than are small goldfish. Most of these observations of the action of urethane were confirmed in as many as fifty experiments.

Ether does not make a good anesthetic for the study of the recovery process under the conditions in which it was used, because the recovery period in tap water is so short. However, several important experiments were performed which will be reported here because of their bearing on the question of the mode and site of action of sodium citrate. A 1% solution of sodium citrate just acid to litmus was prepared; 12 cc of anhydrous ether were added to the solution. Two goldfish were placed in this solution; one of the fish was affected strongly almost immediately. It lost all of its liveliness and balance after a short period of excitation. After ten minutes it had nearly stopped visible breathing movements. Eighteen minutes after immersion in the solution all visible respiratory movements had ceased. The fish was put in tap water in which it recovered in two minutes. The second fish required 32 minutes to become anesthetized; this fish was placed in a 2% solution of sodium citrate just acid to litmus. It required 19 minutes to recover. In no other case of ether anesthesia was anything like such a long recovery period observed. In other experiments with ether the recovery period was always of the order of three minutes. Another experiment was performed in which ten cc of ether were dissolved in two liters of tap water. Two fish were kept in this solution until all visible signs of respiration had disappeared. There was less dyspnea when the fish were subjected to ether-water anesthesia than when the anesthetic bath contained sodium citrate. One was transferred to tap water to recover; the process required three minutes. The other fish was placed in the 2% sodium citrate solution; it recovered in one and one-quarter minutes.

So, fish did not recover in a 2% sodium citrate solution from anesthesia in a sodium citrate-ether-water bath nearly so rapidly as they did in water. Yet, fish anesthetized in a bath containing ether and water recovered more rapidly in a 2% solution of sodium citrate than they did in plain water. The fish re-

covered in water in the same time independently of which anesthetizing bath was used. The time for the induction of anesthesia in the two solutions was of the same order. If sodium citrate was acting to peptize the substrate that is agglomerated by the ether, it should have taken considerably longer for the fish to become anesthetized in the sodium citrate-ether-water solution than in the ether solution. This was not the case. Further, if the above were the case the fish would have recovered more rapidly than it did in sodium citrate after being narcotized in the sodium citrate-ether-water bath. So, the sodium citrate was not acting as a peptizing agent. Still the sodium citrate was not acting as a strong agglomerating agent for the substrate most affected by ether, because fish recovered more rapidly from plain ether anesthesia in a 2% sodium citrate solution than they did in tap water. The data do not offer any evidence that the sodium citrate and ether were acting upon the same substrate. The explanation of the results seems to be that the sodium citrate stimulated the fish by precipitating calcium salts thus arousing it from the light anesthesia that it had undergone. In the case of the fish that was subjected to sodium citrate-ether-water anesthesia the sodium citrate brought about stimulation by the precipitation of calcium salts while the fish was still in the anesthetic bath; so that immersion in sodium citrate after the induction of anesthesia did not revive the fish quickly. The fish in the sodium citrate-ether-water bath came to the top of the solution very shortly after being placed in the bath; there was distinct evidence of loss of balance. This is an indication that the sodium citrate was operating upon the sense organs on the outside of the fish, causing a slight agglomeration there. Also, it undoubtedly acted to agglomerate the slime on the outside of the fish. So, the theory of reversible agglomeration has not met defeat.

In another experiment 15 grams of magnesium sulphate (an anesthetic) were dissolved in a liter of water and five cc of ether added to the solution. Two fish were placed in the solution. Eighteen minutes later they were on their sides at the surface of the water. One became anesthetized in 22 minutes and the other in 31 minutes. Each of the fish was put into tap water upon becoming anesthetized. The fish that was anesthetized first recovered in four minutes; while the other fish recovered in four and one-half minutes. As they do in sodium citrate solutions, these fish exhibited a loss of balance. The recovery time was slightly longer in both cases than that which was observed in several experiments in which ether alone was the anesthetic. This experiment illustrates two things. In the first place, the magnesium sulphate deepened the anesthesia, as a result of its own agglomerating action. Secondly, from the loss of balance and the rise to the surface, agglomeration in the peripheral sense organs can be inferred. Calcium precipitation may have played a part here.

Mention has been made of the fact that a long series of experiments was performed with urethane as the anesthetic. In urethane solutions the usual stimulation corresponding to the initial stages of agglomeration is observed. It would be redundant to set down the experimental details of all of the work on urethane anesthesia and the process of recovery therefrom; for that reason,

except in some special cases, only the general results will be cited. Most of these results have been checked several times, thus eliminating the factor of biological variation. The general procedure was to anesthetize the fish in a 0.5 or 0.75% solution of urethane in tap water. In order to make more nearly certain that the anesthesia was uniform in depth, the fish were left in the urethane solution from two to seven minutes after voluntary movement had ceased and the fish no longer responded to mechanical stimulation with a glass rod. It will be remembered that the recovery phenomenon apparently was not affected by a 20 minute sojourn in the anesthetic bath after the induction of anesthesia.

It was demonstrated that a 2% solution of sodium citrate at an $[H^+] = 1 \times 10^{-8.46}$ reduces the recovery time very greatly. In such a solution the recovery time varies between 30 seconds and two and one-half minutes. Upon removing the fish from the sodium citrate solution and placing them in tap water a period of hyperexcitability is noticed. This is followed by a short depression. The phenomenon is qualitatively the same as that observed under similar conditions using amytal for the anesthetic. The quantitative difference is probably due to the difference in depth of anesthesia, that produced by amytal being much deeper. Under special conditions urethane anesthesia and the recovery therefrom can be prolonged greatly. As has been pointed out, the citrate part of the molecule is responsible for the precipitation of calcium probably largely in the peripheral nerves of the fish, an accompanying phenomenon being agglomeration on the outside. This stimulation results in more rapid recovery of the fish.

Likewise, it was found that a 2% solution of sodium tartrate revives the fish more rapidly than they return to normal in tap water. The recovery is not so rapid as that brought about by sodium citrate. Hyperexcitability is not noticed when the fish are returned to tap water after being in sodium tartrate; but there is a very short period of depression. Now, sodium tartrate is next to sodium citrate in the lyotropic series. That means that its agglomerating action on the peripheral part of the fish will be less than that of sodium citrate. So it appears that calcium precipitation is not the whole story. Sodium tartrate acts both to precipitate calcium and produce a slight peripheral agglomeration. It should be pointed out that this agglomeration produces stimulation because it is so slight, just as the first stage of anesthesia is that of stimulation.

Now, with magnesium citrate we have an agglomerating cation as well as an agglomerating anion. As a result placing fish anesthetized by urethane in a saturated solution of magnesium citrate delays their recovery.

In a series of experiments using a 0.75% solution of urethane to produce anesthesia and eighth-molar solutions as recovery media, it was demonstrated that sodium bromide increases the rate of recovery from the anesthesia. It did not work so rapidly as sodium citrate and sodium tartrate; however, there is no question but that sodium bromide is a peptizing agent. In this case, there can not be agglomeration produced by the sodium bromide under ordinary conditions so far as one can see. It seems reasonable to assume, therefore,

that sodium bromide acts to peptize the substrate that is agglomerated by the urethane.

The calcium-precipitating action of the sulphate radical of sodium sulphate was manifested in one experiment. In this case the fish recovered rapidly in a solution of that salt. Another experiment failed to show this up very clearly.

A study of the cations, still using eighth-molar solutions, revealed the fact that aluminum chloride apparently brings the fish out of anesthesia more rapidly than sodium chloride, which in turn is more effective than calcium chloride. This situation requires elaboration. The calcium chloride solution killed three out of four of the fish after they apparently had recovered from the anesthesia. One fish hemorrhaged in the solution. The order of recovery time was approximately: Al_2Cl_6 , $1\frac{1}{2}$ minutes; NaCl , 4 minutes; CaCl_2 , $8\frac{1}{2}$ minutes. The case of sodium chloride is not out of the ordinary; the chloride ion acts as a peptizing agent to hasten the recovery. With calcium chloride we have a weak agglomerating cation, therefore the delay in recovery. Fish generally recover from urethane anesthesia in about this length of time when placed in tap water. The calcium ion can be assumed to be acting to stimulate by a slight agglomeration on the outside of the fish. With aluminum chloride the situation is slightly different, for the trivalent aluminum ion appears to cause quite a bit of stimulation by agglomeration of protein colloids in the peripheral sense-organs. Upon transferring the fish from the aluminum chloride solution to tap water, hyperexcitability is noticed. The fish swim rapidly and blindly at the surface of the water. They are not so apt to become excited while in the aluminum chloride solution as when they are in a sodium citrate solution. The fact that the aluminum ion acts to stimulate the fish on the outside rather than acting directly to lessen the narcosis can be illustrated by an experiment with sodium amytal as an anesthetic and aluminum sulphate as the recovery agent. The anesthetic solution was prepared by dissolving one and one-half grams of sodium amytal in a liter of water and adding eight cc of 0.236 N HCl. The fish was placed in M/20 aluminum sulphate solution; after 11 minutes, it did not appear to have recovered. Upon being transferred to tap water, the fish began to swim around at the surface in circles touching the side of the container. It continued to do this for a couple of hours, around and around, always in the same direction, never leaving the side of the container, never ceasing to swim. Normal fish do not perform that way. So, it appears that aluminum sulphate and sodium citrate stimulate anesthetized fish without necessarily bringing them back to normal, when the anesthesia is deep.

Two fish were anesthetized in a 0.5% solution of urethane; they were left in the solution for four minutes after the induction of anesthesia. The fish were then placed in a very dilute solution of sodium sulphate, one or two small crystals of the salt in a liter of water. The fish were shocked intermittently using four volts, direct current, the application being made with wide aluminum electrodes. Each shock stimulated the fish and caused it to wriggle and swim a short distance. It became continually more sensitive to the current. At the end of three minutes it continued to swim without the shocks. The second fish responded in the same manner, taking four minutes to recover.

So, by electrical stimulation fish can be wakened abnormally rapidly from urethane anesthesia; and electrical stimulation probably does not result in peptization.

Using a 1% solution of urethane to anesthetize fish, it was demonstrated that the fish recover more rapidly in Ringer's solution than in distilled water. This is presumably due to the peptizing action of the chloride ion. Likewise, fish anesthetized in a 3.5% solution of urethane dissolved in Ringer's solution recovered more rapidly in an isotonic sodium chloride solution than they did in distilled water.

Approximately isotonic solutions of sodium tartrate, sodium rhodanate and aluminum sulphate were prepared, using as a basis 0.9% sodium chloride solution, and used as recovery media. The recovery phenomena were not essentially different from the observed effect of eighth-molar solutions. From this it can be concluded that osmotic pressure differences do not play an essential rôle in the recovery process.

Experiments were performed in which the anesthetic was injected into the fish. By way of illustration, 0.5 cc of a 10% solution of urethane was injected into the peritoneal cavity of an 8-gram fish. The fish was anesthetized deeply in 11 minutes. It did not recover from the anesthetic in 78 minutes. Thus, the anesthesia was much deeper than is usual when urethane is dissolved in the water. Other experiments were performed in which the fish were deeply anesthetized by a 0.75% solution of urethane, dissolved in Ringer's solution and isotonic salt solutions were injected to produce recovery. Not enough experiments were performed to be certain of the results. Fish of approximately equal weight were used. In each case 0.5 cc of the isotonic salt solution was injected. Sodium rhodanate produced excitement in the fish most quickly, one minute; aluminum sulphate required three minutes; and sodium tartrate required four minutes. With no injection the fish recovered in four minutes. The recovery of the fish injected with aluminum sulphate was not attended by circular swimming. So, the action of this salt internally appears to be different from its action externally.

Fish anesthetized by sodium amytal became wildly excited after one minute in a 0.1 M solution of sodium carbonate. There was further great excitement when the fish was transferred to water. Here we have both calcium precipitation and peptization by hydroxyl ions. Two more transfers to the sodium carbonate solution resulted in death. Another fish made a good and rapid recovery in a 0.1 M sodium salicylate solution.

Now, if calcium precipitation is largely responsible for the stimulating action of sodium citrate, reducing the amount of calcium in the fish should result in diminishing the action of that salt in producing the artificial recovery from anesthesia that has been described. Also, if the calcium-precipitating action is reduced, the agglomerating action of sodium citrate should become more apparent and sodium rhodanate should be more effective than sodium citrate in bringing the fish out of anesthesia. In an attempt to realize these predictions, fish were placed in a bowl; and distilled water was run in continuously for a period of about five days. A total of more than 54 liters of

distilled water was run through. The fish container was a 1-liter beaker. The fish were not fed during the process in order to avoid the introduction of calcium. The first fish subjected to this process died in convulsions in about four days. It may be that a tetany similar to parathyroid tetany resulted from lowering the calcium content of the fish. The second time that the process was carried out Ringer's solution, without calcium and magnesium chloride, was used to "dialyze" the fish on the second and third day; distilled water was used the rest of the time. Fish that were so treated were anesthetized in a 0.75% solution of urethane. It was noticed that the anesthesia was quite a bit more profound than usual. When the anesthetized fish were placed in sodium citrate (1.78% solution just acid to litmus) the phenomenon was more like that described under amytal anesthesia. The fish apparently aroused from the anesthesia, and became narcotized again when placed in distilled water. However, there was no great excitement noticed. In several experiments it was found that the 1.78% solution of sodium citrate, when it was slightly alkaline and when it was slightly acid, did not counteract the anesthesia for from 22 to 24 minutes. The fish were artificially stimulated in a shorter time than that; but they lapsed back into a good narcosis. The artificial stimulation indicates that the "dialyzing" process did not lower the calcium sufficiently. In other recovery experiments with these specially treated fish an eighth-molar solution of sodium rhodanate revived them three to five minutes more rapidly than the sodium citrate solution did. So, the peptizing action of sodium rhodanate was demonstrated clearly, and it was shown that sodium citrate indirectly stimulates fish to bring them out of anesthesia.

It was found possible to show that sodium citrate has an anesthetic-like action on these specially treated fish and that sodium rhodanate tends to counteract it. Two of the fish were placed in the above sodium citrate solution for a period of four minutes. They were highly excited in the sodium citrate solution. When transferred to distilled water they became depressed. Their sensitivity to touch was diminished; and the fin movements were incoordinated as in anesthesia. After nine minutes in tap water, when the fish were again normal in action, they were placed in the sodium citrate solution again, where they were left for four minutes. One fish then was put in water and the other in eighth-molar sodium rhodanate solution. Two minutes later the fish in sodium rhodanate was excitable to touch and was swimming around; while the other fish appeared to be anesthetized. This is not a very striking experiment; but it is definite; and sodium citrate is not a good anesthetic.

General Conclusions

1. A study of anesthesia and the recovery phenomena has been made on goldfish anesthetized by sodium amytal, ether, nembutal, alcohol, and urethane.
2. A comparison of the anesthesia produced by these compounds is made.

3. At first sight the theory of reversible agglomeration does not appear to hold because sodium citrate, sodium tartrate, and aluminum sulphate all revive the fish more rapidly than sodium rhodanate, sodium chloride and sodium bromide. Sodium salicylate and sodium carbonate also revive fish quickly.

4. Sodium bromide, sodium chloride, and sodium rhodanate all bring the fish out of anesthesia more rapidly than tap water due to the peptizing action of the anions.

5. Electric shocks bring fish out of anesthesia more rapidly than is normal.

6. Sodium citrate acts on a different substrate from that which is agglomerated by anesthetics.

7. Sodium citrate precipitates calcium, coagulates the slime on the fish, and causes agglomeration of protein colloids in some of the sense organs on the outside of the fish. This causes the fish to become stimulated, and apparently awakens them from the anesthesia.

8. Fish awakened from deep anesthesia by the stimulation produced by sodium citrate, become narcotized again when placed in tap water.

9. Aluminum sulphate stimulates fish by its agglomerating action in the outside sense organs. Fish revived by the use of aluminum sulphate behave abnormally when placed in tap water. Still the total time for recovery is short.

10. Fish that are "dialyzed" in distilled water go under deeper anesthesia in urethane than fish not so treated.

11. Fish that have been "dialyzed" in distilled water recover from urethane anesthesia more rapidly in a sodium rhodanate solution than in a sodium citrate solution.

12. Fish that have been "dialyzed" in distilled water behave as though anesthetized when placed in sodium citrate solutions. Sodium rhodanate appears to counteract this effect.

13. Osmotic pressure changes do not appear to be concerned in the recovery from anesthesia. Likewise, slight variations in acidity do not seem to make any difference.

14. Claude Bernard's theory of anesthesia has been substantiated again.

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VISCOSITY AND MOLECULAR WEIGHTS OF POLYMERIC MATERIALS*

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The existence of an intimate relationship between the viscous behavior of colloidal solutions and their ultramicroscopic physical structure has long been acknowledged, but, with the exception of simple dilute suspensions to which Einstein's equation is applicable, it has not in general been possible to deduce quantitative conclusions concerning colloidal structure from viscosities. Although a number of different factors and conditions have been recognized as important—e.g., (1) aggregation, (2) electroviscous effects, (3) solvation, and (4) non-spherical particle-shape—the evaluation of the significance of each in a given case has usually been a matter of speculation. The influence of aggregation on viscosity has frequently been demonstrated by direct microscopic or ultramicroscopic examination of sols in which the particles are discernible and it is probably often significant also for the characteristic viscous behavior of lyophilic sols. Electroviscous effects, like electrokinetic phenomena in general, are restricted to conducting systems. Solvation has undoubtedly been over-emphasized in the past, for independent and, presumably, reasonably reliable estimations of the degree of solvation frequently fail to confirm the very high values deduced from viscosities. Although the effect of particle-shape should in special cases be calculable from hydrodynamic theory, no careful analysis was made until very recently. At our request Professor L. Onsager¹ has kindly worked out the case of a suspension of rotation-ellipsoids and has found that the shape factor of Einstein's equation (which is 2.5 for spheres of any size) increases with the square of the ratio of major to minor axes. The detailed calculations are, however, not yet available.

In the absence of a theoretical basis for taking particle-shape into consideration, efforts have been made to obtain empirical relations.² Of especial interest are the results of Staudinger and his associates for a number of natural and synthetic macromolecular substances, such as cellulose, rubber, and their derivatives, polystyrene, polyvinyl compounds, etc. These substances are typical, linear, high-molecular-weight polymers, and belong to the general

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¹ Washington meeting, American Physical Society, April 28-30, 1932; Physical Bulletin 7, No. 2, p. 7. By a less rigorous analysis, R. Eisenschitz: *Z. physik. Chem.*, **158**, 78 (1931), reached the conclusion that, as a first approximation, the shape factor in Einstein's equation increases linearly with the ratio of the major-to-minor axes of ellipsoidal particles.

² H. Staudinger: *Kolloid-Z.*, **51**, 74; **53**, 19 (1930); **54**, 129 (1931); *Z. angew. Chem.*, **45**, 276 (1932); *Ber.*, **65**, 267 (1932), and many earlier papers; H. Fikentscher and H. Mark: *Kolloid-Z.*, **49**, 135 (1929); H. Mark: **53**, 32 (1930); H. Fikentscher: *Cellulosechemie*, **1932**, 58.

class of intrinsic colloids.¹ According to Staudinger, these substances pass into solution, in the absence of association, as single, rod-like molecules, and their high specific hydrodynamic volumes² are a consequence of the molecular form. For solutions of a given concentration and polymeric series, the viscosity was found to be proportional to the molecular weight (up to several thousand) and, therefore, to the length of the rod-like molecules. By extrapolation of empirical relationships established on low polymers, to which ordinary molecular-weight methods are applicable, Staudinger has estimated the molecular weights of many high polymers, including rubber and cellulose.

Since there are relatively few satisfactory general methods for determining the molecular weights of high polymers or for studying the nature of their solutions, Staudinger's conclusions are of great interest and his methods deserve careful examination. As a test of his methods, this paper presents results on a polymeric series of considerable range for which the molecular weights are believed to be known exceptionally accurately. It will be shown that Staudinger's equations only approximately describe the facts and must be used with caution. Molecular weights assigned by Staudinger to rubber, cellulose, cellulose derivatives, and very high polymers in general may be considerably in error, and are probably too high rather than too low, as he supposes.

Staudinger's Viscosity vs. Molecular-Weight Equations

Staudinger has employed two methods for calculating molecular weights from viscosity measurements on dilute solutions of the polymers.

Method I depends on the equation

$$(1) \log \eta_r = K_{cm}Mc$$

where η_r is the relative viscosity compared to that of the solvent, K_{cm} is the "molecular weight-concentration constant"³ and is specific to a given solvent and polymeric series, M is the molecular weight, and c is the concentration, which is usually expressed by Staudinger in terms of "base-molarity," i.e., the molarity of the recurrent group constituting the structural unit of the polymer. K_{cm} was evaluated from viscosity measurements on the lower members of the series, for which the molecular weights could be determined by the usual methods. The molecular weights of the higher polymers were then calculated from the viscosities of their solutions by extrapolation, using the above equation.

Method II depends on the equation

$$(2) \eta_r - 1 = K_m Mc$$

where K_m is a constant specific to the solvent and polymeric series. As Hess and Sakurada⁴ have pointed out, this equation is not independent of equation

¹ E. O. Kraemer and G. R. Sears: *J. Rheology*, **2**, 292 (1931).

² E. O. Kraemer and G. R. Sears: *J. Rheology*, **1**, 231 (1930).

³ Staudinger, in effect, writes the constant of proportionality $1/K_{cm}$ instead of K_{cm} , but there is no apparent object in using the reciprocal form.

⁴ K. Hess and I. Sakurada: *Ber.*, **64**, 1183 (1931).

1, but is equivalent to the first two terms of the expansion of equation 1 when natural logarithms are used, K_m being then equal to K_{cm} . Equation 2 is to be used only at low concentrations where the relative viscosity is a linear function of concentration. It is in this respect equivalent to Einstein's equation, in which, however, $K_m M$ is constant and equal to 2.5 when c is expressed as a volume fraction. In this method also, K_m is evaluated by measurements on members of the series with known molecular weights.

The Viscosities of Polymeric ω -Hydroxydecanoic Acids

For investigating the relation between viscosity and molecular weight more accurately than has hitherto been done, a series of polymers of the general formula $\text{HO}[(\text{CH}_2)_9\text{COO}]_x\text{H}$, formed by intermolecular esterification of ω -hydroxydecanoic acid, was selected because of the possibility of determining

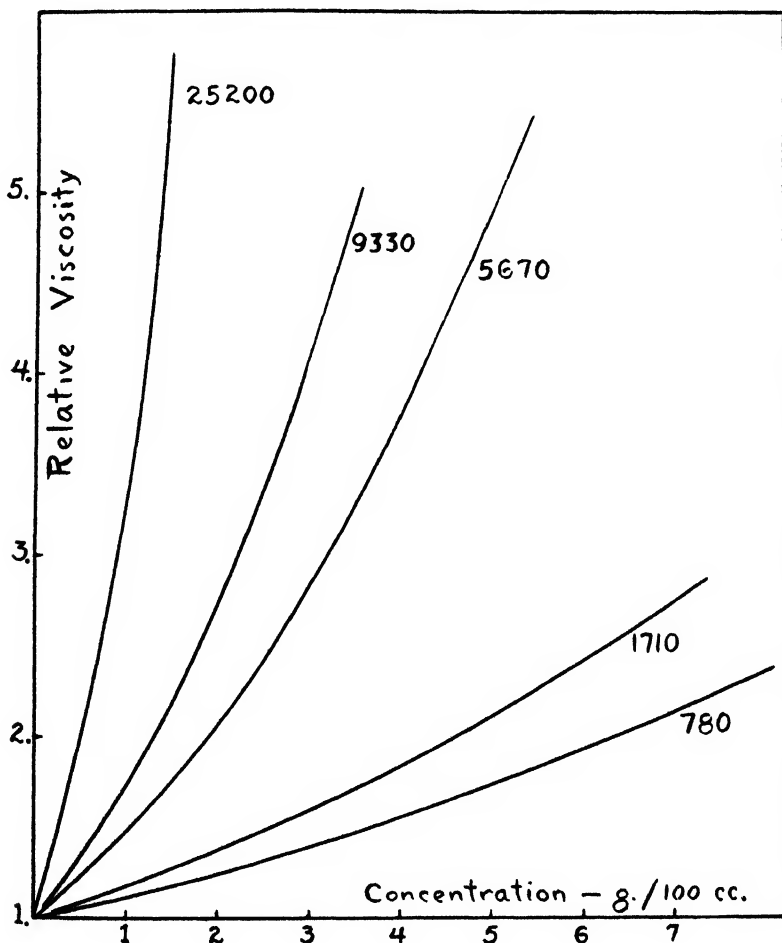


FIG. 1

Influence of Molecular Weight upon the Viscosity-Concentration Curves for Polymeric ω -Hydroxydecanoic Acids

TABLE I
Viscosity of Polymeric ω -Hydroxydecanoic Acid in
sym.-Tetrachloroethane

Mol. Wt.	Wt. %	25°C.			50°C.	
		Density	g/100 c.c.	η_r	Density	η_r
780	0.2596	1.5816	0.4106	1.0449	1.5431	1.0370
	0.5174	1.5788	0.8169	1.0894	1.5408	1.0757
	1.747	1.5680	2.739	1.3583	1.5303	1.3015
	3.088	1.5559	4.804	1.7077	1.5185	1.5773
	5.158	1.5372	7.929	2.3536	1.5013	2.0896
1,710	0.1028	1.5826	0.1626	1.0245	1.5438	1.0223
	0.2532	1.5814	0.4004	1.0663	1.5423	1.0625
	1.311	1.5715	2.060	1.3950	1.5330	1.3414
	2.718	1.5588	4.236	1.9053	1.5210	1.7493
	4.591	1.5419	7.079	2.7949	1.5051	2.4606
5,670	0.1719	1.5820	0.272	1.1172	1.5432	1.1078
	0.3399	1.5805	0.5372	1.2409	1.5416	1.2196
	0.8568	1.5770	1.351	1.6425	1.5371	1.5951
	1.687	1.5697	2.647	2.5843	1.5313	2.3773
	3.436	1.5524	5.335	5.3302	1.5164	4.6341
9,330	0.05051	1.5832	0.07997	1.0495	1.5445	1.0458
	0.1025	1.5827	0.1622	1.1023	1.5438	1.0969
	0.4264	1.5797	0.6735	1.4772	1.5409	1.4337
	0.8598	1.5759	1.355	2.0759	1.5371	1.9657
	1.388	1.5711	2.181	3.0036	1.5327	2.7625
16,900	2.228	1.5634	3.483	4.9055	1.5254	4.3871
	0.02221	1.5837	0.03517	1.0357	1.5448	1.0333
	0.04434	1.5835	0.07021	1.0770	1.5447	1.0713
	0.01589	1.5839	0.02516	1.0344	—	—
	0.03226	1.5836	0.05108	1.0670	—	—
25,200	0.01671	1.5838	0.02647	1.0452	1.5445	1.0418
	0.01717	1.5838	0.02720	1.0507	1.5445	1.0477
	0.04276	1.5835	0.06771	1.1233	1.5444	1.1143
	0.04365	1.5835	0.06912	1.1368	1.5444	1.1305
	0.08583	1.5831	0.1359	1.2497	1.5440	1.2317
	0.1709	1.5821	0.2703	1.5316	1.5431	1.4970
	0.3447	1.5806	0.5449	2.2208	1.5417	2.1210
	0.6026	1.5781	0.9508	3.2335	1.5393	3.0401
	0.9443	1.5754	1.488	5.7649	1.5373	5.2436

the molecular weights by titration of the terminal acid groups.¹ In this way higher molecular weights could be determined than by the customary physico-chemical methods. The values so determined satisfactorily checked values obtained ebullioscopically on the lower members; the value for the highest

¹ These polymers were prepared and fractionated by one of us (F.J.V.N.) in connection with polymerization researches with Dr. W. H. Carothers, and will be described in greater detail in a separate paper.

polymer was confirmed by ultracentrifugal analysis (titration, 25,200; centrifugal sedimentation equilibrium, 27,000).¹ Admittedly the polymers are not entirely homogeneous with respect to molecular weight. The ultracentrifugal analysis, for instance, indicated the presence of some material having a molecular weight above 27,000 and a small portion of smaller molecular weight. The uniformity was distinctly greater, however, than was expected, and was, we believe, probably quite as good as for the polymers of equal molecular weight that were used by Staudinger. Unfortunately, Staudinger gave no information concerning uniformity as definite as that obtainable with the ultracentrifuge.

The viscosities of dilute solutions in *sym.*-tetrachloroethane were accurately measured at 25 and 50° C. with a Bingham capillary viscometer. The results are presented in Table I and Fig. 1, and are discussed under the following topics.

Log Relative Viscosity vs. Molecular Weight (Staudinger's Method I)

The logarithms of the relative viscosities at 25° were plotted against the concentrations in grams per 100 cc. of solution. As usual for high-molecular-weight materials, the curves were in all cases concave to the concentration

TABLE II

Mol. Wt.	(log η_r)/ c_0	$K_{cm} \times 10^4$ *
780	0.0484	10.5
1710	0.0702	7.0
5670	0.173	5.2
9330	0.261	4.8
16900	0.452	4.5
20600	0.574	4.7
25200	0.778	5.2

* K_{cm} is defined by equation 1 when concentration is in terms of base-molarity, and corresponds to the reciprocal of Staudinger's K_{cm} constant.

axis,² and, accordingly, could not be expressed by equation 1. The limiting slope at zero concentration therefore was determined for each curve (graphically), the values being given in Table II, column 2. In column 3 are given the values of K_{cm} , obtained from the values of column 2 by division by the molecular weight and multiplication by 17, the factor 17 being necessary to convert the concentrations to Staudinger's base-molar basis.

According to Staudinger, K_{cm} should be a constant, characteristic of a particular polymeric series and solvent. The values given in Table II suggest that K_{cm} reaches a constant value of about 5×10^{-4} near a molecular weight of 5,000, on the basis of which the higher molecular weights might be roughly calculated by equation 1.

¹ We are indebted to Dr. W. D. Lansing of this laboratory for the ultracentrifugal analysis.

² J. W. McBain, C. E. Harvey and L. E. Smith: J. Phys. Chem., 30, 312 (1926); H. Fikentscher: Cellulosechemie, 1932, 58.

As a matter of fact, however, the variation in K_{cm} above a molecular weight of 5,000 distinctly exceeds the experimental error, and the calculation of K_{cm} simply confuses the actual relationship between viscosity and molecular weight. This becomes evident when $(\log \eta_r)/c_0$ is plotted against molecular weight. The curve is indeed practically linear for molecular weights below 17,000, but it does not extrapolate through the origin, as required by equation 1. For molecular weights exceeding 17,000, an upward curvature becomes detectable, i.e., $(\log \eta_r)/c_0$ gradually increases more rapidly than the molecular weight. If the curvature continues with increasing molecular weight, as seems likely, the discrepancy between the actual viscosity and the viscosity calculated from equation 1 becomes greater with increasing molecular weight.

Since there is greater theoretical justification for using a linear equation relating viscosity and concentration (equation 2), and since, as pointed out above, equations 1 and 2 are essentially identical for low concentrations, a more detailed discussion of the results is left for the following section.

Relative Viscosity vs. Molecular Weight (Staudinger's Method II)

The influence of particle shape and structure on viscosity is most simply revealed at very low concentrations, where mutual interference of the particles is negligible. Under these conditions, the relative increase in viscosity over that of the solvent is directly proportional to the concentration.

The relative viscosities for the lowest concentrations (Table I) were plotted against concentration on a large scale. Although a slight departure from linearity could be detected for the highest polymers, rather accurate values for the slopes at zero concentration ($= (\eta_r - 1)/c_0$) could be obtained. This quantity may be termed the "specific increase in relative viscosity," and its values are given in Table III, column 2 (for 25°) and column 3 (for 50°C.), c being expressed in grams of solute per 100 cc. of solution. According to equation 2, the ratios of these slopes to the corresponding molecular weights should be constant, as well as the K_m values (column 4), obtained by multiplying these ratios by 17 (a base-molar solution of hydroxydecanoic acid polymer containing 17 g./100 cc.). The K_m -values are directly comparable to Staudinger's K_m -values. The average of the ratios of corresponding K_m 's and K_{cm} 's is 2.37, instead of 2.30 as required theoretically by the relationship between equations 1 and 2 when Briggsian logarithms are used in connection with equation 1.

TABLE III

Mol. Wt.	$(\eta_r - 1)/c_0$ (for 25°)	$(\eta_r - 1)/c_0$ (for 50°)	$K_m \times 10^4$ (25°C.)
780	0.109	0.093	23.7
1710	0.157	0.145	15.6
5670	0.425	0.403	12.7
9330	0.615	0.586	11.2
16900	1.04	1.00	10.5
20600	1.32	—	10.9
25200	1.84	1.75	12.4

The K_m -values show a systematic drift like that of the K_{cm} -values of Table II. A similar drift is evident in Staudinger's data for polyvinyl acetate,¹ polystyrene,² and cellulose acetate.³ With the highest hydroxydecanoic acid polymers an approximately constant value of 12×10^{-4} appears to be attained, which is the same as that found by Staudinger⁴ for cellulose and cellulose acetate, but distinctly larger than the values for paraffin hydrocarbons (0.85×10^{-4}), polystyrenes (1.8×10^{-4}), rubber and hydorrubber (3×10^{-4}), polyoxymethylenes (2.2×10^{-4}), and polyvinyl acetates (3×10^{-4}). As Staudinger has shown, the differences in the K_m 's for different polymeric series are to a first approximation related in a simple way to the length of the recurring unit in the polymeric chain. Specifically, when n is the number of atoms per recurring unit in the polymeric chain, the ratio K_m/n is approximately constant; i.e., $K_m/n = K_{eqv}$. To the extent that equation 2 is applicable, this means that the relationship between viscosity and molecular weight is the same for different polymeric series when concentrations are expressed in terms of molarity of chain-atoms (i.e., nc). For the case of the hydroxydecanoic acid polymers, n equals 11, and K_{eqv} equals 1.1×10^{-4} . This is thus not greatly different from the values found by Staudinger for hydrocarbons in tetralin or benzene (0.85×10^{-4}), hydrocarbons in carbon tetrachloride (1.14×10^{-4}), polyoxymethylene in chloroform (1.1×10^{-4}), cellulose in cuprammonium and cellulose acetate in *m*-cresol (2.4×10^{-4}).

On the whole, therefore, the hydroxydecanoic acid polymers show the same relations between viscosity and molecular weight as Staudinger has described for other linear polymers of low and intermediate molecular weight (up to about 10,000). However, the applicability of these relations by extrapolation to the estimation of the molecular weights of high polymers is a matter requiring closer scrutiny of the data for its justification. Two principal points are involved: the accuracy with which the relationship between viscosity and molecular weight is known over the range of molecular weights that can be measured by reliable methods, and the probability that the empirical relationship holds far outside the range in which it is experimentally established.

With respect to the first point, reference was made above to the approximate constancy of K_m for molecular weights above 5000. As a matter of fact, however, the inconstancy of K_m is definitely greater than the experimental error, and equation 2 does not accurately represent the facts. The relation between $(\eta - 1)/c_0$ and molecular weight is more adequately shown graphically (Fig. 2), whereupon it is evident that the relation is indeed a linear one over a rather wide range of molecular weight, but not one of simple proportionality. Whereas the inconstancy of K_m would suggest an anomalous situation at low molecular weights, the curve reveals no such thing. The significance of the marked variation in K_m at low molecular weights and of the attainment of

¹ Ann., **488**, 16 (1931).

² Ber., **63**, 222 (1930).

³ Ber., **63**, 3132 (1930).

⁴ Ber., **65**, 267 (1932).

approximate constancy at higher molecular weights is obvious. Up to molecular weights of about 17,000, the curve is represented by the equation¹

$$(3) \quad (\eta_r - 1)/c = 0.065 + 5.85 \times 10^{-5} M$$

when concentrations are in grams per 100 cc.

Above 17,000, however, a distinct upward curvature becomes evident, and equation 3 also fails to be applicable. The calculation of molecular weights of hydroxydecanoic acid polymers in the range of 100,000 or higher by equations

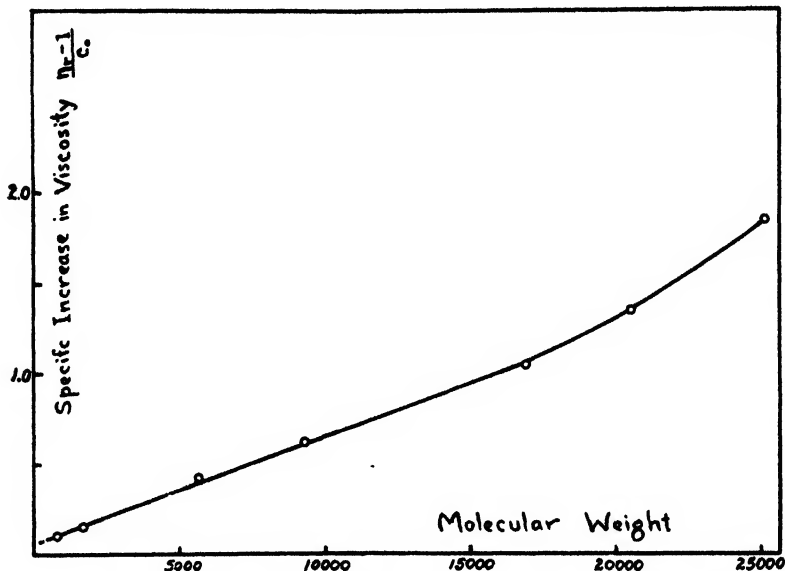


FIG. 2

Specific Increase in Viscosity vs. Molecular Weight for ω -Hydroxydecanoic Acid Polymers

2 or 3 from viscosity data would obviously give quite erroneous results. The selection of a non-linear empirical equation for use in extensive extrapolations would be too arbitrary to be useful in a case of this sort.

Whether the results presented here should be considered typical of linear polymers, it is not possible to say with definiteness, but there is no apparent *a priori* reason why they should be considered exceptional. It is true that Staudinger and his associates have not described similar results. In most cases, however, Staudinger's molecular weights, determined cryoscopically, become decidedly unreliable above 10,000 (for which freezing-point depressions of less than 0.01° were measured) and values of K_m were usually calculated from data below 15,000. It seems possible, therefore, that the linear relationship shown below 15,000 would break down at higher molecular weights for some of the polymeric series studied by Staudinger as well as for the hydroxy-

¹ Equation 3 is identical in type with that used by Staudinger and Ochiai: *Z. physik. Chem.*, 158, 35 (1931), in taking account of the effect of end groups.

decanoic acid series. Although the departure from linearity might not take the form of an upward curvature as in Fig 2, it would in general seem desirable to admit the possibility of departure from linearity at high molecular weights unless definite evidence to the contrary was available. Linear relations over very wide ranges of the variables involved are after all rather exceptional. It is interesting and suggestive to carry out calculations involving wide extrapolations, but it seems to us unfortunate and almost without precedent to assert definitely and positively, as Staudinger does, without any theoretical and very little experimental support, that a linear relation established between molecular weights of 0 and 15,000 must hold in the range of 150,000 and over. While granting that Staudinger's calculations indicate that rubber, cellulose, their derivatives, and certain synthetic polymers like polystyrene have very high molecular weights, we consider the numerical values as possibly a good deal in error, and probably too high.

Fikentscher's Equation

Fikentscher (*loc. cit.*) has recently proposed an equation containing a single arbitrary constant, which, although empirical, appears to be superior in general applicability to any hitherto used: namely

$$(4) \quad \log \eta_r = \frac{75 k^2 c}{1 + 1.5kc} + kc$$

where c is the concentration in grams per 100 cc of solution and k is the arbitrary constant, which Fikentscher calls the "eigenviskosität."

In order to determine the relationship between k and molecular weight, the k 's were calculated for the hydroxydecanoic acid polymers. Suitably rearranging equation 4 and setting $c = 0$ gives $\log \eta_r/c_0 = 75 k^2 + k$, with which the values of k may be conveniently calculated from the values of $(\log \eta_r)/c_0$ given in Table II. The k 's are given in Table IV, column 2. The curve of k against molecular weight is concave to the molecular weight axis and rather strongly curved. It consequently does not provide a satisfactory substitute for equations 2 and 3 for determining the molecular weights of high polymers by extrapolation.

In passing, attention may be called to columns 4 and 5 illustrating the success with which Fikentscher's equation reproduces the observations on the hydroxydecanoic acids. When k is selected to fit the viscosities of dilute solutions, as in the present case, the calculated viscosities for more concentrated solutions may differ considerably from the observed values. The discrepancies are not so glaring if the constant k is calculated from the viscosities of the concentrated solutions. For instance, the calculated and observed viscosities for the low concentrations of the highest polymer agree to about 5 per cent when k is calculated from the data on the most concentrated solution. It is of interest to note that the k for the highest hydroxydecanoic acid polymer is about equal to the k 's found by Fikentscher for "medium viscosity" nitrocellulose in acetone and for rayon in cuprammonium.

TABLE IV

Mol. Wt.	k	Concn.	Obs. η_r	Calc. η_r
780	0.020	7.929	2.35	2.19
1710	0.025	7.079	2.79	2.68
5670	0.042	5.335	5.33	5.58
9330	0.058	3.483	4.91	5.66
16900	0.071	—	—	—
20600	0.081	—	—	—
25200	0.0954	0.1	1.19	1.19
		0.5	2.05	2.32
		1.0	3.42	4.93
		1.5	5.85	9.68

Temperature Coefficient of Viscosity

An important argument in support of the view that the unit in solutions of linear polymers is the single unsolvated molecule is provided by the fact that the relative viscosity is affected but slightly by changes in temperature. As may be seen in Table V, the ratio of $(\eta_r - 1)/c_0$ at 25° and 50° is practically

TABLE V

Mol. Wt.	780	1710	5670	9330	16900	25200
Temp. Coeff.	1.17	1.08	1.05	1.05	1.04	1.05

constant for all except the lowest polymer and differs but little from unity. The departure from unity may be due to a small solvation effect.

Effect of Rate of Shear

A characteristic feature of the viscosity of solutions of high polymers, particularly those with a large specific hydrodynamic volume, is their failure to show a constant viscosity at different rates of shear. In general, the variation in viscosity with rate of shear increases with the concentration and the specific hydrodynamic volume. As the concentration is reduced, the magnitude of the effect may become too small to detect, but it probably does not completely disappear. For the highest concentrations of the highest polymer used in this investigation, an increase in pressure from 97 to 530 g./cm.² caused a drop in viscosity of about 3%. In other cases, the effect was less, and could be disregarded for the purposes of this investigation. It is not to be denied, however, that this is a significant property of macromolecular solutions.

Experimental Details

Preparation of Materials: The polymeric ω -hydroxydecanoic acids were prepared by heating the monomer at various temperatures and pressures for different times, depending upon the degree of polymerization desired. The polymers were fractionally crystallized to increase the homogeneity. The

molecular weights were determined by titration of chloroform-alcohol solutions of the polymers with alcoholic potassium hydroxide.

The tetrachloroethane was washed with water, dried and redistilled. It was characterized by the following properties: boiling range, 143.5-144° at 76 cm.; density $d_4^{25} = 1.5842$; $N_D^{25} = 1.4920$; absolute viscosity at 25° = 0.01610 poises. Its viscosity remained unchanged during the course of the investigation.

The solutions were made up by weight and the densities were determined pycnometrically. Since a detectable decrease in viscosity of the solutions, especially of the higher polymers, occurs during a few days, the viscosities were measured on fresh solutions.

Viscometry: The viscosities were measured in accordance with Bingham's procedure for accurate viscometry.¹ The viscometer was of the standard Bingham type and had the following dimensions: capillary length, 9.85 cm.; average effective radius (calculated from the efflux time for the standardizing liquid), 0.01512 cm.; efflux volume, 3.963 cc. The construction of the viscometer was reasonably symmetrical, the efflux times for the two directions of flow differing by but a fraction of a percent. The two times were therefore averaged.

The constants of the instrument were determined by calibration with gas-free water at 25° and 50°C. The kinetic-energy instrument constant was obtained from the variation of efflux time with pressure by Knibb's method (see Bingham's book). In the equation $\eta = c\pi t - c'd/t$, $c = 5.206 \times 10^{-7}$ and $c' = 0.0309$. The kinetic energy correction rarely amounted to 1% of the total pressure for measurements at 25° and seldom exceeded 2% at 50°.

The efflux times were measured with two checked 0.1-second stop watches. The time was never less than 150 seconds at 25° or 100 seconds at 50°, and usually was considerably greater.

The pressures were read on mercury or dibutyl phthalate manometers, depending on the magnitude of the pressure, with a steel tape graduated in millimeters. The difference in level was never less than 12 cm. and was usually considerably greater. The customary corrections were applied for expansion of the tape, buoyancy, etc.

The temperatures of the two thermostats used were held at $25^\circ \pm 0.03$ and $50^\circ \pm 0.03$, as determined by a thermometer with Bur. Stand. certificate. After determination of the mean efflux time at 25°, the viscometer was transferred to the 50° thermostat without refilling, the volume was readjusted, and effluxes at 50° observed. Occasionally, the viscometer was again returned to the 25° bath to assure reversibility.

During filling of the viscometer, the solutions were filtered through a sintered glass disc under conditions effectively preventing evaporation of solvent or contamination from the air. Evaporation was also guarded against while the efflux times were being determined.

In general, the inconsistency of the results was less than 0.2%.

¹ E. C. Bingham: "Fluidity and Plasticity" (1922).

Summary

Careful measurements of the viscosities of solutions of polymeric hydroxy-decanoic acids with molecular weights from 780 to 25200 inclusive show that a simple relationship exists between viscosity and molecular weight over a wide range of the latter, in qualitative agreement with observations of Staudinger for numerous polymeric series. The quantitative expression of the relationship, however, requires a modification of the Staudinger equation. In the range of high molecular weights (above 15,000) the simple relationship breaks down for the polymeric ω -hydroxydecanoic acids. In the light of these results, Staudinger's values for the molecular weights of rubber, cellulose, and other very high polymers are unreliable.

ADSORPTION OF OXALIC ACID BY ALUMINA

BY PHILLIP H. DEWEY

When studying the oxidation of acetaldehyde by hydrogen peroxide in presence of an alumina catalyst made from aluminum nitrate, there was an apparent loss of acetaldehyde. Since acetic acid and oxalic acid are the two most probable oxidation products, some experiments were made with acetic acid and oxalic acid to determine whether there was any difficulty in analyzing for them in presence of alumina. Acetic acid can be washed out of the alumina without difficulty and titrated with alkali. This is not possible with oxalic acid. A solution containing 20 g Al_2O_3 , 100 cc H_2O and 0.36 g oxalic acid was allowed to stand for six days and was then extracted for twenty-seven hours in a Soxhlet apparatus. Titration showed 0.0153 g oxalic acid, less than five percent of what should have been found.

This might have been due to the formation of an insoluble oxalate or to very strong adsorption. Runs were therefore made with acetic acid and with oxalic acid. The results are shown graphically in Fig. 1. It is clear that no compound is formed in either case and that oxalic acid is adsorbed very strongly at the low concentrations. At the higher concentrations there is enough alumina peptized to give an almost gelatinous precipitate when neutralized with caustic soda. In cases where the precipitate is at all marked, the determination of the oxalic acid in solution gives low results when titrating with alkali, using phenolphthalein as an indicator. The end-point is indefinite, the first pink appearing at a value as much as forty percent low in the case of a 0.015 M solution. If the titrations are made hot and alkali enough is added to give a permanent pink when boiled for two minutes, the proper value is obtained.

It is possible to determine the free and adsorbed oxalic acid with the regular hot acid permanganate titration.

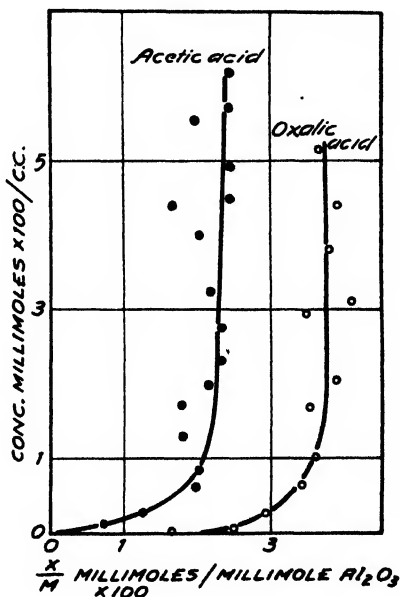


FIG. 1
Adsorption Curves for Oxalic and Acetic Acids

● Curve II Acetic Acid
○ Curve I Oxalic Acid

Summary

1. Acetic acid and oxalic acid form no compounds with an alumina catalyst at room temperature.
2. Oxalic acid is adsorbed much more strongly than acetic acid by an alumina catalyst.
3. Oxalic acid cannot be washed out of alumina in any reasonable time.
4. Oxalic acid adsorbed by alumina can be determined satisfactorily by the hot acid permanganate titration.

This work was done under the direction of Professor Bancroft.

Cornell University.

A MODIFIED ELECTRO ULTRAFILTER

BY D. VON KLOBUSITZKY

The electro ultrafilter of Bechhold,¹ which, as is known, gives a rapid dialysis, at the same time concentrating the solution, is for that reason of the greatest utility in the laboratory for chemical and physical chemistry purposes, but it has for us the inconvenience of being made with an apparatus of porcelain Bechhold-König only manufactured in Germany. This makes it necessary to buy spare parts or in the case of breakages to interrupt the work for some time. The first alternative is very expensive and the second retards the work. My end therefore was to construct an electro ultrafilter with easy mounted parts in common use.

For model I used a large Bechhold electro ultrafilter with suction in only one direction. As a recipient for the solution I used a strong glass cylinder having at one of its extremities a neck. This recipient was closed with a membrane of parchment tied with a thread to stop the entrance of

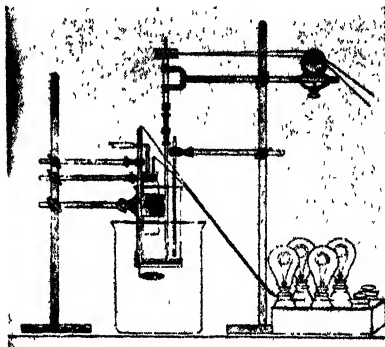


FIG. 1

water (when it was necessary I waxed or covered the outer side of the parchment with a layer of a liquefied mixture of wax and colophony). In this recipient was placed a porcelain candle of any make. This candle was completely glazed with the exception of the bottom and closed with a rubber stopper containing two bores, to one of which was connected an electrode of platinum which went to the bottom and to the other a glass tube in the form of an L reaching also to the bottom. The wall at the bottom of the candle was, as in the Bechhold-König recipient, in the first place placed in a solution of 10% collodion in acetic acid and afterwards hardened and washed in water until all traces of acetic acid had disappeared. Thus the two recipients remained impermeable to colloids.

Below the parchment membrane was placed an electrode of silver: in the glass recipient an agitator and thermometer: all the apparatus was remaining in a vessel containing distilled water. A continual current of the maximum 110 volts and 0.5 amperes was connected: the positive pole to the interval platinum electrode and the negative pole to the end of the silver electrode. A tube in the form of an L was connected to a tap of water. The reaction of the solution dialysed could be regulated by the intensity of the suction.

¹ H. Bechhold: *Z. physik. Chem.*, 60, 257 (1907).

When the colloid solution contained a large quantity of electrolytes it was necessary to augment the distance of the silver electrode from the parchment membrane to avoid warming and so coagulating.

With regards to the remaining characteristics the method of dialysing and the functional capacities were equal to the apparatus of Bechhold.

The mounting of the apparatus can be seen from the sketch, Fig. 1.

Summary

An article on an apparatus for an electro ultrafilter easily mounted and for common use.

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NEW BOOKS

Liesegang Rings and Other Periodic Structures. By Ernest S. Hedges. 22 × 16 cm: pp. viii + 122. London: Chapman and Hall, 1932. Price: 10 shillings, 6 pence. Well-known monographs on the above subject have been published by Liesegang, E. Küster and others, and there have been sections devoted to it in the textbooks of colloidal chemistry. This is the first book on the subject written in the English language.

The very considerable interest that has been aroused in the subject among chemists and also among biologists and botanists can be clearly traced in the complete bibliography that is included by Dr. Hedges in this volume. This ranges from 1896, when the first paper was published by Liesegang, up to the present date. This bibliography alone will prove of the greatest service to all interested, and especially to those wishing to carry out original research on some aspect of this subject.

Dr. Hedges has a first chapter giving a brief account of those aspects of colloidal chemistry a knowledge of which is necessary for a comprehension of the later chapters of the book. He gives an account of the main experimental facts under such headings as, influence of various conditions, variations of structure, chemical analysis of structure, etc. There is included an interesting account of periodic structures produced in capillaries from the interaction of both gases and liquids and of periodic diffusion structures produced without chemical reaction. There is a chapter on periodic structures obtained on crystallisation, evaporation, condensation, sedimentation, etc., and a short but very interesting account of natural periodic structures.

A comprehensive and critical treatment is given of the many theories that have been put forward to account for these phenomena. To many this section of the book will be considered its most valuable feature; the literature on this subject has become so bulky, 270 papers having been published in the last ten years, and the experimentation is frequently of such a character, that it is difficult to correctly appreciate the true scientific implication of the results. In the opinion of the reviewer anyone reading this delightful book of Dr. Hedges will conclude that we are very far yet from any comprehensive theory which is more than qualitative in character. There is therefore a very definite need now for this book which should stimulate research in the direction of a mathematical theory.

The book is well printed and there are some beautiful illustrations.

D. C. Jones

A Short Course in Qualitative Analysis. By F. E. Brown. 20 × 13 cm; pp. xiii + 332. New York City: The Century Company, 1932. Price \$2.25. Another text on Qualitative Analysis has been added to the long list of those already published within the last five or ten years. Very little in the way of new methods has been presented, and such a text would be uncalled for if it were not for the fact that each instructor must teach Qualitative Analysis with the aim in view of adapting his course to the students' previous training in chemistry.

This book has been developed from the author's mimeographed notes used, with revision from time to time, by approximately 3000 students. It is without doubt admirably suited for large classes of students who have not had a full year of beginning chemistry. The course as outlined is planned for a quarter of eleven weeks, following two quarters of General Chemistry. The experimental part of the course requires about sixty hours of actual laboratory work and should be accompanied by two lectures or recitation periods per week.

Part I, Theory, includes 146 pages and is divided into ten chapters as follows: Solutions, Ionization, Reversible Reactions and Equilibrium, Mass Law and Solubility Product, Hydrolysis, Oxidation and Reduction, Types of Reactions and the Writing of Equations, Amphoteric Hydroxides, Complex Ions, The Colloidal Condition. This part of the text is well written and contains enough theory for a thorough understanding of the analytical procedure. Several sections are devoted to the development and explanation of the Mass

Action equation and its corollary the Solubility Product equation. In addition the Solubility Product equation is developed mathematically from the standpoint of Ionization from Crystals. The author gives two general types of chemical reactions, one in which no change of valence takes place and the other involving valence change. These general types are further divided into nine subdivisions. Numerous questions and problems conclude each chapter in this section. They cover thoroughly the important parts of the chapter and should give the student a fair idea of what he is expected to know.

The second part of the text, comprising 65 pages, is devoted to Preliminary Experiments on the basic and acidic radicals. They involve the actual separations and tests which are used later in the scheme of analysis. These simple experiments with questions related to them should enable the student to analyze an unknown substance intelligently and correctly.

Part III deals with the ordinary scheme of analysis for the usual cations and anions. This scheme is so arranged as to make the tests as fool-proof as possible and to eliminate all unusual and expensive apparatus, dangerous chemicals, etc. The author states that he has omitted fusions since they are unsatisfactory in porcelain crucibles and nickel or platinum is too expensive to use with large classes. Therefore no test for silicates is included.

The appendix contains a table listing the ordinary properties of the common inorganic compounds for each cation studied in the course. In addition it contains directions for preparing reagents, test solutions, etc.

Throughout the text the author has succeeded beyond our expectations in bringing together theory and practice. It appears that his aim has been, as it should be in any short course, to stress a complete understanding of what is being done rather than the actual performance of the task. He has given extended illustrations of the theory which might seem unnecessary to the instructor but which are exceedingly valuable to a freshman. However, in certain sections he appears to be inconsistent. After explaining the Mass Action and Solubility Product equations, on page 85 he proceeds to write $\text{C}_2\text{H}_3^+ \times \text{C}_2\text{O}_4^{2-} = K_{sp}$. We ordinarily think of the Solubility Product equation as being applied to saturated solutions of slightly soluble substances. The chapters on Oxidation and Reduction and the Writing of Equations would be more appropriate near the beginning of the book. Many students know little or nothing about writing equations when they start Qualitative Analysis. The sooner they learn it the better.

The procedure used for the analysis of the alkaline earth group has proven unsatisfactory in the experience of the reviewer. Complete precipitation of barium as chromate cannot be made in acetic acid solution without the addition of an alkali acetate. Flame tests are used for final identifications here as well as in the tests for sodium and potassium. Flame tests are unsatisfactory in the hands of beginning students, especially when the separations are somewhat incomplete. The alkaline earth metals may be separated and identified, without resort to flame tests, if the proper precautions regarding concentrations, digestion, and general manipulation are observed. The use of paranitro-benzeneazoresorcinol in the test for magnesium is a decided improvement over the classical magnesium ammonium phosphate test.

A few typographical errors appear throughout the book. The first sentence in the introduction fails to make sense. On page 16 the formula of sodium sulphate is written NaSO_4 , so consequently the equation is unbalanced.

The book as a whole is a valuable addition to our Qualitative Analysis texts, and many instructors should find it well adapted to the courses which they teach.

Alfred W. Avenas

Elektrolyte. By Hans Falkenhagen. 26×18 cm; pp. xvi+346. Leipzig: S. Hirzel, 1932. Price: 23 mark unbound; 24.8 marks bound. The rapid development in the theory of electrolytes which has followed the mathematical investigations of Debye and Hückel has given rise to an extensive literature which is distributed through many journals in different languages. The importance of the subject has made the need of a comprehensive survey of the whole field obvious to all physical chemists, and it is therefore very satisfactory that Prof. Falken-

hagen, who has made important contributions to the study of electrolytes, should have brought together so much material in a compact, uniform, and systematic treatise. The classical theory is treated briefly yet adequately, in particular the thermodynamic foundations and equations required in the development of the new theory are deduced, and a uniform system of notation is a considerable aid to the comprehension of the subject. The theory of activity is then dealt with in a very clear and sufficient manner, and on page 74 the reader is fully prepared to begin the study of the behaviour of strong electrolytes. A good account of the effects of field strength and frequency on the conductivity of electrolytes provides an experimental foundation for the fundamental conception of interionic forces. It appears that an effect not taken into account by the theory of Debye and Hückel may make itself felt with high field strengths, viz., the ionisation by collision which formed the basis of the explanation offered by Larmor and by the reviewer many years ago for the anomalies of strong electrolytes. Although this effect is not adequate to account for the deviations with ordinary field strengths, it seems as if it must be taken into account in a complete theory of conductivity. The theory of strong electrolytes, both from the point of view of thermodynamics and also of conductivity, follows. In this part the mathematical treatment is full and clear, although a few misprints are troublesome and it is sometimes difficult to trace the origin of equations used owing to neglect of cross references in a few cases. Where so much care has been taken to make the whole intelligible it is a pity that in a few cases the thread has been lost in this way. The section on conductivity is more difficult, partly on account of the inherent difficulty of the subject and partly by the use of vector notation where it is not necessary. The very general development of this part of the subject, which cannot be followed up in detail, is no doubt valuable from the point of view of the mathematician, but the chemist will miss here what he might have been led to expect from the earlier part of the book, that is, a gradual development of the theory from the simple case, which is after all nearly all the theory is competent to attack at present, to the more general treatment.

The extensions of the Debye-Hückel theory to more concentrated solutions made by Hückel, Bjerrum, Gronwall, LaMer and Sandved, are dealt with in a very satisfactory manner and the evidence of incomplete ionisation is also fully considered. This part of the book is especially valuable. The book closes with an account of the method of statistical mechanics due to Fowler, in which some misprints may offer difficulty to some readers. This method, although superficially more general than that of Debye and Hückel, is really not so, since the Boltzmann and Poisson equations both appear in it. It is interesting exercise in elementary mathematics but goes no deeper than the usual method.

This book gives a comprehensive and authoritative survey of the theory of strong electrolytes, including recent experimental researches, and may be recommended to physical chemists. It goes much further than any other collected accounts which have appeared, and brings the whole subject up to the modern standpoint.

J. R. Partington

Lehrbuch der physikalischen Chemie. By Karl Jellinek. Vol. IV, Part 2. 25 × 17 cm; pp. 289-624. Stuttgart: Ferdinand Enke, 1932. Price. 30 marks. The comprehensive treatise of Jellinek is planned to fill five volumes, of which three have been published complete and part of the fourth has appeared. It is an excellent work, carefully planned, clearly and accurately written, and comprising not only what is probably the best account of the theory of the subject which has yet appeared but also a wealth of numerical data and description of experimental methods which makes it invaluable in the laboratory. The general plan resembles that of Ostwald's famous *Lehrbuch*, of which it may be considered the modern successor. The present publication forms the second installment of the fourth volume and begins and ends with an incomplete sentence. The first 17 pages complete the section on electrolytic equilibria of the preceding issue and the rest deals with the theory of concentrated mixtures (solutions). This is divided into three parts, the first (53 pages) dealing with gas mixtures, the second (267 pages) with liquid mixtures, and the third (half a page at the end) beginning the treatment of mixed crystals. The first two sections are complete.

They deal with equations of state, thermal magnitudes and thermodynamics, chemical equilibria and electro-chemistry, including fused salts. As in other parts of the work, the mathematical parts are very clear and the equations derived are capable of direct experimental application. The experimental methods are fully described and the apparatus figured, and the numerical results are collected and tabulated. The references to the literature are numerous, and include American work. The volume is a welcome contribution to the literature of physical chemistry and should be in every chemical library.

J. R. Partington

Über eine neue Klasse von Verbindungen des positiv einwertigen Jods. By *Heinrich Carlsöhn*. 24 × 16 cm; pp. iv + 63. Leipzig: S. Hirzel, 1932. Price: 2.50 marks. In this monograph the author describes the preparation and properties of a new class of complex compounds in which electropositive univalent iodine stabilised by coordination with pyridine functions as a salt forming radical.

Two types of these iodine coordination compounds are recorded, in one of which the iodine is coordinated with two molecular proportions of pyridine and in the other with one molecular proportion of this base. The former complex, which is the less stable, is produced by the action of iodine on a solution of an argentous or mercurous salt in the presence of pyridine.



In addition to the foregoing nitrate salts of this dypyridino-iodine complex have been obtained with other strongly electronegative anions such as the perchlorate, sulphate and hydrogen sulphate.

Derivatives of the more stable monopyridino-iodine complex are formed by the action of iodine or argentous salts of organic acids in presence of pyridine.



In these complexes X represents such acidic radicals as the acetate, benzoate, nitrobenzoate and benzoate. Similar compounds are described with dibasic acidic radicals, for instance, the oxalate, succinate and phthalate. A chloride and a bromide of this series are also indicated.

The physical properties of these complex iodine derivatives have been closely studied including solubility in organic solvents and electrical conductivity measurements which support the structural formulae, $[\text{I} \cdot 2\text{py}] \text{X}$ and $[\text{I} \cdot \text{pyX}]$ for the two types each involving a coordination number of two for the pyridino-iodine complexes.

When a solution of the nitrate $[\text{I} \cdot 2\text{py}]\text{NO}_3$ is electrolysed the iodine is liberated exclusively at the cathode and this decomposition in conjunction with the fact that many metals displace iodine from these complex salts reveals the electropositive character of the iodine atom.

Considerable space (pp. 9-15) is devoted to analytical methods and a new gravimetric estimation of pyridine as the salt $[\text{Cr}(\text{CNS})_4 \cdot 2\text{NH}_3] \cdot \frac{1}{2} \text{H} \cdot \text{py} \cdot \frac{1}{2} \text{H}_2\text{O}$ of Reineck's acid is described.

The results might, however, have been described more concisely and analytical details should preferably have been summarised in a short appendix.

G. T. Morgan

Tables of Cubic Crystal Structure of Elements and Compounds. By *I. E. Knaggs, B. Karlik and C. F. Elam*. 25 × 16 cm; pp. 90 + blank pages for notes. London: Adam Hilger, Ltd., 1932. Price: 11 shillings, 6 pence. Roughly twenty years have elapsed since W. L. Bragg's pioneer work indicated the atomic arrangement in the cubic crystals NaCl and KCl. Since then the subject has grown enormously, becoming at once a new branch of physics, chemistry and mineralogy with a large literature of its own. The efficiency of the research worker is very much increased if there is available a reliable handbook summarising the results of previous work. The present summary of cubic crystal structure by Drs. Knaggs, Karlik and Elam, although admittedly not a rival, follows closely on the much more comprehensive "Strukturbericht" of Ewald and Hermann and should prove useful to those who have not access to this work. The book is divided into two parts, the first of which sets out

the chemical formulae of the inorganic and organic substances dealt with and gives key numbers to further tables containing structure details, and full bibliographical references. Part II, contributed by Miss Elam, is a valuable summary of work on alloys belonging to the cubic system. A useful feature is the arrangement of crystal structures in order of lattice spacing. The lists of references are complete up to August 1931 and the tables are well printed on good paper. Considering the limited scope of the work, its price seems rather high.

The letter P, used extensively throughout the tables as a lattice symbol, appears to be confused with the letter S of the explanatory introduction. A fuller use of the new nomenclature enabling characteristic co-ordinates of atoms in the more complicated cells to be read off would have added to the value of the tables. A minor error is the use of Wo for W on page 80 and authors' initials are incorrectly given in bibliography A, references 106, 107 and 356.

J. T. Randall

Volumetric Analysis. By G. Fowles. 20 × 13 cm; pp. xii + 202. London: G. Bell and Sons, 1932. Price: six shillings. This textbook of Volumetric Analysis is written for students and teachers who are concerned with any examination from the School Certificate to the University Honours Degree. It presents therefore an elementary survey of the subject from a theoretical and practical standpoint, and then proceeds to deal in an excellent way with both the older methods of analysis and most of the recent methods that have been thoroughly tested. It contains sections on such physico-chemical principles as are involved in the theory of indicators, oxidation and reduction methods and precipitation processes. The advanced section of this book presents in an admirable way all the volumetric methods which a student would be required to know for an Honours Chemistry Examination, the author evidently having carefully performed the estimations himself. This book, as the author intends, would certainly lead to many of the older processes being superseded by more accurate and frequently also more rapid methods. Adsorption indicators, titanium reduction processes, and the use of liquid amalgams for the reduction of compounds of certain metals are some of the modern improvements dealt with. Some examples of the use of ceric sulphate might usefully have been included.

This book can be recommended confidently to schools, and students brought up on it would find it an admirable textbook even beyond their Honours stage. On the other hand, in the opinion of the reviewer, other textbooks, including both volumetric and gravimetric analysis and excluding the elementary teaching contained in the earlier part of this book would be preferred as a University textbook for a student reading for an Honours degree in Chemistry.

D. C. Jones

Gmelins Handbuch der anorganischen Chemie. Edited by R. J. Meyer. System-number 59, Section B, Part 5. Eisen. Eighth edition. 25 × 17 cm; pp. 873-1165. Berlin: Verlag Chemie, 1932. Price: 53 marks (subscription price 47.50 marks). The issue of part 5 completes section B of the chemistry of iron, i.e. the portion dealing with its compounds, and a title page and detailed list of contents accompanies the part. The ferricyanides and ferrocyanides of various metals, the ferrites and ferrates, double chlorides and sulphates, are included in this part. The treatment is comprehensive and modern work appears to be fully covered. Numerous tables and phase rule diagrams are included. The five parts of number 59 of the new Gmelin give the most complete account of the chemistry of iron compounds in existence.

J. R. Partington

Gmelins Handbuch der anorganischen Chemie. Edited by R. J. Meyer. System-number 58, Section A, Part 2. Kobalt. Eighth edition. 25 × 17 cm; pp. 221-502. Berlin: Verlag Chemie, 1932. Price: 48 marks (subscription price 42 marks). The issue of this part completes the chemistry of cobalt in the new Gmelin and deals with the compounds of that element. Although many complex compounds, such as cobaltic cyanides, are dealt with, the cobaltammines are not included. There is a section on the colour and constitution of cobalt salts. The treatment, as was to be expected, is very detailed yet concise and the two parts of number 58 form a comprehensive survey of the chemistry of cobalt.

J. R. Partington

Die Valenzzahl und ihre Beziehungen zum Bau der Atome. By H. Lessheim and R. Samuel. (*Fortschritte der Chemie, Physik und physikalischen Chemie*). Vol. XIX, No. 3. 24 × 16 cm; pp. 98. Berlin: Gebrüder Borntraeger, 1927. Price: 6.40 marks. This small monograph gives a general and elementary account of atomic structure from the point of view of Bohr's theory; of the construction of the Periodic System in terms of atomic structure; of the types of valency; of the interpretation of spectra; and of the chemical properties of the atoms as a consequence of their constitution. The part dealing with quantum numbers, which is based on Pauli's principle, is very clear and could usefully supplement any works on the electronic theory of valency which are deficient in this respect.

J. R. Partington

Protoplasmic Action and Nervous Action. By Ralph S. Lillie. Second edition. 19 × 14 cm. pp. ix + 417. Chicago: The University of Chicago Press, 1932. Price: \$3.00. The first edition appeared in 1923 and was reviewed (28, 1001 (1924)). "In this edition some additional references, chiefly to recent books and articles of comprehensive or summarizing nature, have been added at the ends of the chapters. Certain changes in theory or interpretation made necessary by the progress of research, are also briefly indicated." In other words the book is essentially of 1923 and not of 1932. That is a pity because what was good then is not good now.

There is nothing to show, for instance, that Claude Bernard's theory of narcosis is the only one possible now. This is the more remarkable because the author came very close to formulating it himself in 1923.

"Certain definite changes in the physical properties of protoplasm, analogous in many respects with those produced by salts, have been observed in various cases to accompany the action of narcotizing compounds; these changes indicate that underlying narcosis there are definite modifications of the structural conditions in protoplasm; and presumably it is to such modifications that the changes in physiological properties and activity are to be referred," p. 206.

"During narcosis there appears very generally to be a decrease of permeability, an increase in the resistance to structural breakdown or cytolysis, and an increase of protoplasmic viscosity. From the general nature of these changes it would seem that the structural substratum of the living matter assumes temporarily a denser or physically more stable condition," p. 207.

This would have led to reversible agglomeration of living tissue and all its attendant consequences long before the reviewer got into the game if the author had had the courage to think things through. Unfortunately, he followed the line of least resistance.

Warburg and Wiesel also noted "that all of these compounds [alcohols, urethanes, ketones] in sufficient concentration caused precipitation in the press-juice [of yeast], and that the orders of relative precipitating effectiveness and anticatalytic action were the same; this order is also that of relative narcotic action. This parallelism between precipitating action and narcotic action recalls Claude Bernard's hypothesis that a partial coagulation of protoplasmic constituents [proteins] is the essential condition of narcosis. With the living cell, however, much lower concentrations are required to stop fermentation than with the enzyme solution, so that the parallel between the inactivation of the structureless enzyme solution and the inhibition of fermentation in the living cell is not complete. This difference may indicate the importance of the vital organization as such, or it may depend on the presence of special compounds (lipoids) in the living cell," p. 227.

Wilder D. Bancroft

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